Computer Physics Communications 280 (2022) 108490

Contents lists available at ScienceDirect

Computer Physics Communications

www.elsevier.com/locate/cpc

Calculation of atomic integrals between relativistic functions by means of algebraic methods[☆],[☆☆]

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ARTICLE INFO

Article history:
Received 26 November 2021
Received in revised form 29 July 2022
Accepted 3 August 2022
Available online 12 August 2022

Keywords:
Atomic integrals
Numerical stability
PNC amplitude
Algebraic methods

ABSTRACT

We propose the use of Sturmian basis set for relativistic atomic structure calculations. We describe a numerically stable algebraic calculation of one- and two-particle radial integrals. The method is illustrated on the basis set independent calculation of energies, electric dipole moments, hyperfine integrals and parity non-conserving (PNC) amplitude for Cs in Dirac-Hartree-Fock approximation with frozen core orbitals. The previously reported results for electric dipole moments and PNC amplitude are found to be strongly basis dependent.

Program summary
Program title: PASC
CPC Library link to program files: https://doi.org/10.17632/xycmhhcr5h.1
Licensing provisions: MIT
Programming language: Fortran 2008
Nature of problem: Precise atomic measurements require reliable and highly accurate atomic structure calculations. Here we deal with the problem of numerical stability of the atomic integrals and basis set independence of the calculations.
Solution method: The radial parts of the electronic orbitals are expanded in a discrete Sturmian functions that are eigenfunctions of one of the generators of the so(2, 1) Lie algebra. This algebraic structure is used to deduce algebraic relations between the radial parts of the atomic integrals. This leads to numerically stable calculation, which in turn allows to achieve basis set independence.
Additional comments including restrictions and unusual features: The method is currently restricted to the Dirac-Hartree-Fock method. However, this limitation will be lifted in future versions, which will be extended with the coupled clusters method.

1. Introduction

Atomic physics is still at the frontier of our exploration of fundamental physical laws [1]. In particular, the comparison of theory and experiment for parity non-conserving (PNC) interactions in heavy atoms represents a stringent low-energy test of the Standard Model complementing the high-energy experiments [1–6]. However, for the case of Cs atom, where PNC amplitude has been most accurately measured [7], there has been controversy regarding theoretical evaluation of the effect [1,2]. The first step in clarifying the situation is to establish the independence of the result on the used basis set.

When dealing with atoms, one first takes advantage of their spherical symmetry and by means of the angular momentum algebra integrates out the spinor-angular degrees of freedom. This is now a standard exercise. One is then left with the radial degree of freedom only. This can be dealt with either numerically, see e.g. [8–10], by confining the atom to an artificial cavity and replacing the continuous radial variable by a set of discrete points, called the radial grid, or analytically by expanding the wave function into a basis set. The most popular choice for the latter is a B-spline basis, see e.g. [11–15], where one again confines the atom to an artificial cavity. The radial coordinate is divided into segments, and in each segment the radial part of the atomic function

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[☆] The review of this paper was arranged by Prof. N.S. Scott.
[☆☆] This paper and its associated computer program are available via the Computer Physics Communications homepage on ScienceDirect (http://www.sciencedirect.com/science/journal/00104655).
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https://doi.org/10.1016/j.cpc.2022.108490
0010-4655/

is expanded into piecewise polynomials. Finally, there is a third possibility: to expand the radial part of the atomic function into a complete and entirely discrete set, the so-called Sturmian basis set, see e.g. [16,19,20]. Moreover, this basis is orthonormal [21], albeit with the weight r^{-1} with respect to the ordinary weight, and thus avoids the problem of basis set linear dependence.

As it should be clear, the numerical and B-spline approaches are very similar. They both start to lose their appeal when one deals with highly excited states since then the interval where one needs an accurate numerical description of the wave function becomes too large. Also, they both require to enclose the atom in an artificial cavity. Thus, when removing artificial restrictions, necessary for carrying out the numerical calculation, to obtain physical observables, one has to make sure of the independence of the result on number of parameters, such as the volume of the artificial cavity, the number of finite intervals the cavity is decomposed into, number of the basis functions or density of grid used on each of the finite intervals, etc. This could be problematic for second-order quantities when summation over complete system of atomic states is required. On the other hand, the Sturmian functions form an orthonormal basis set on an infinite interval with only one artificial parameter, namely the number of the considered basis functions. Indeed, the most accurate non-relativistic calculations of positions and widths of highly doubly excited states in helium [22], single and double photoionization of helium [23], and so on, were done with the use of this basis set.

The problem with using Sturmian functions is numerically stable calculation of the matrix elements of the electrostatic interaction between highly excited atomic configurations. This problem is common to expansion into any orthogonal basis set. The orthogonality requirement enforces functions to have a large number of nodes. Straightforward integration of these functions based on their explicit coordinate representation in double or even quadruple precision arithmetics very quickly yields numerical results that are completely off the correct values. A solution to this problem was developed in [16] for the non-relativistic case. Its key idea is to consider Sturmian functions not “analytically”, i.e. through their explicit functional form, but “algebraically”, i.e. as functions satisfying certain recursion relations. These recursion relations then imply recursion relations for the integrals of these functions. In this paper we extend this method to the relativistic case and further improve it. Calculation of the matrix elements of the electrostatic interaction is separated in the standard way, i.e. by means of the multipole expansion of the Coulomb potential, into spinor-angular and radial integrations. The radial integrals are evaluated as follows: first the product of two Sturmian functions is expressed as a linear combination of Sturmian functions, where the coefficients of the linear combination satisfy a certain difference equation in two variables. This reduces the radial integrals over four functions to integrals over two functions. Second, calculation of these reduced integrals is transformed into the solution of difference equations in one variable. Third, we find the asymptotic form of the one-variable difference equations. This in turn yields numerically stable solution of these equations for very large quantum numbers.

The paper is organized as follows. In Section 2 we introduce the analytic restricted Dirac-Hartree-Fock (DHF) method for closed-shell atoms. One-particle orbital functions are expanded into the product of spinor-angular and radial functions. The spinor-angular functions are constructed from the eigenstates of the total angular momentum, parity and non-Hermitian, but $\mathcal{PT}$-symmetric [17], operator introduced long time ago by Biedenharn [18]. The radial functions are expanded into the relativistic Sturmian basis set. In the following Sections 3 and 4 we describe calculation of the needed one-particle integrals and spinor-angular integration of two-particle integrals, respectively. These Sections are preparation for the main objective of this paper: in Section 5 we propose an algebraic method for the calculation of the radial part of the two-particle integrals. In Section 6 we briefly outline the calculation of PNC amplitude in Cs in the frozen core approximation. The practical implementation of the method in Fortran is described in Section 7. Section 8 gives the reader a brief idea about the PASC program and its structure. The performance of the method is discussed in Section 9; conclusions are drawn in Section 10. In Appendices we describe the evaluation of the specific types of the hypergeometric function and derive difference equation for special one-electron integrals. These technical issues are needed in main Section 5.

2. Restricted Dirac-Hartree-Fock method for closed-shell atoms

2.1. Restricted Dirac-Hartree-Fock model

In the restricted DHF model we put N electrons into N spin-orbitals labeled by a. These spin-orbitals are successively put in accordance with the Bohr Aufbau principle into ν shells labeled by A. Each shell is characterized by the total (orbital plus spin) angular momentum j_A, relativistic parity κ_A and principal quantum number n_A, the last number distinguishing different shells of the same spinor-angular symmetry. Each shell comprises $2j_A+1$ states of different projections m of the total angular momentum on one of the coordinate axes.

The energy of N electrons in the Hartree-Fock approximation is

$$E=\sum_{a=1}^{N}\langle a|\hat{\mathsf{Z}}|a\rangle+\frac{1}{2}\sum_{a=1}^{N}\sum_{b=1}^{N}\langle a|_1\langle b|_2\hat{\mathsf{V}}\left(|a\rangle_1|b\rangle_2-|b\rangle_1|a\rangle_2\right) \tag{1}$$

where a and b stand for spin-orbitals and $\hat{\mathsf{Z}}$ and $\hat{\mathsf{V}}$ are one- and two-particle operators, respectively. Variation of the energy functional (1) with respect to spin-orbitals a, subjected to normalization constraint $\langle a|\,a\rangle=1$, and setting this variation to zero yields the Hartree-Fock equations

$$\hat{\mathsf{F}}|a\rangle=\mathcal{E}_a|a\rangle\,, \tag{2}$$

where the action of the Fock operator on the spin-orbitals is given by

$$\hat{\mathsf{F}}|a\rangle_1=\hat{\mathsf{Z}}|a\rangle_1+\sum_{b=1}^{N}\langle b|_2\hat{\mathsf{V}}\left(|a\rangle_1|b\rangle_2-|b\rangle_1|a\rangle_2\right) \tag{3}$$

and $\mathcal{E}_a$ are one-particle energies. They are related to the total energy by the relation

$$E=\frac{1}{2}\sum_{a=1}^{N}\left[\mathcal{E}_a+\langle a|\hat{\mathsf{Z}}|a\rangle\right]. \tag{4}$$

The last three relations are completely general and hold regardless of the specific forms of the one- and two-particle operators $\hat{\mathsf{Z}}$ and $\hat{\mathsf{V}}$ and spin-orbitals a.

In the case of the relativistic Hartree-Fock method, also called Dirac-Hartree-Fock (DHF) method, the one- and two-particle operators read in natural units ($\hbar=c=1$)

$$\hat{\mathsf{Z}}=\gamma_0\boldsymbol{\gamma}\cdot\hat{\boldsymbol{P}}+\gamma_0\mu-\frac{Z\alpha}{\hat{\mathsf{R}}} \tag{5}$$

and $\hat{\mathsf{V}}=\frac{\alpha}{\hat{\mathsf{R}}_{12}}$, respectively, where γ's are the Dirac matrices in the standard (Dirac) representation[1] and $\alpha=1/137.0359991$ is

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[1] The explicit form of the Dirac matrices is

$$\gamma_0=\begin{pmatrix}1&0\\0&-1\end{pmatrix},\quad \boldsymbol{\gamma}=\begin{pmatrix}0&\boldsymbol{\sigma}\\-\boldsymbol{\sigma}&0\end{pmatrix},$$

the fine-structure constant [24]. The Fock operator $\hat{\mathsf{F}}$, Eq. (3), then takes the form of the Hamiltonian for a spin-1/2 particle moving in an external spherically symmetric field

$$\hat{\mathsf{F}} = \hat{\mathsf{Z}} + \hat{\mathsf{V}}_e \,, \quad \hat{\mathsf{V}}_e = \sum_{b=1}^{N} \langle b|_2 \frac{\alpha}{\hat{\mathsf{R}}_{12}} (1 - \mathcal{P}_{12}) |b\rangle_2 \,, \tag{6}$$

where $\mathcal{P}_{12}$ exchanges the coordinates of the electrons. Before proceeding further, it is advantageous to subtract the electron rest mass μ from the Fock operator (6) and one-particle energies $\mathcal{E}_a$ and express them in the dimensionless atomic units;

$$\boldsymbol{R} = \frac{\boldsymbol{r}}{\mu Z\alpha} \,, \quad \boldsymbol{P} = \mu Z\alpha \boldsymbol{p} \,. \tag{7}$$

The Fock operator (6) and Hartree-Fock equations (2) then read

$$\hat{\mathsf{f}} = \frac{\hat{\mathsf{F}} - \mu}{\mu (Z\alpha)^2} = \hat{\mathsf{z}} + \frac{1}{Z} \hat{\mathsf{v}} \,, \tag{8}$$

$$\hat{\mathsf{z}} = \frac{1}{Z\alpha} \gamma_0 \boldsymbol{\gamma} \cdot \hat{\boldsymbol{p}} + \frac{\gamma_0 - 1}{(Z\alpha)^2} - \frac{1}{r} \,, \tag{9}$$

$$\hat{\mathsf{v}} = \sum_{b=1}^{N} \langle b|_2 \frac{1}{\hat{\mathsf{r}}_{12}} (1 - \mathcal{P}_{12}) |b\rangle_2 \tag{10}$$

and

$$\hat{\mathsf{f}} |a\rangle = \epsilon_a |a\rangle \,, \quad \epsilon_a = \frac{\mathcal{E}_a - \mu}{\mu (Z\alpha)^2} \,, \tag{11}$$

respectively.

2.2. Integrals of motion and $\mathcal{PT}$-symmetric operator

As is well-known, see e.g. [8], there are three operators commuting with the Dirac Hamiltonian for a particle in a spherically symmetric field: the square, $\hat{\mathsf{J}}^2$, and the third component, $\hat{\mathsf{J}}_z$, of the total angular momentum given by the sum of orbital and spin angular momentum,

$$\hat{\boldsymbol{J}} = \hat{\boldsymbol{L}} + \frac{1}{2} \boldsymbol{\Sigma} \,,$$

and the relativistic parity operator $\hat{\mathsf{K}}$,

$$\hat{\mathsf{K}} = \gamma_0 \left(\boldsymbol{\Sigma} \cdot \hat{\boldsymbol{L}} + 1 \right) . \tag{12}$$

As noted in [18], in the case of a purely Coulomb field, $V_e = 0$ in Eq. (6), another integral of motion appears for the second-order Dirac Hamiltonian. Every solution of the first-order Dirac equation (2), $(\mathcal{E}_a - \hat{\mathsf{F}})|a\rangle = 0$, can be written in the form

$$\langle \boldsymbol{r} |\, a\rangle = [\gamma_0 (\mathcal{E}_a - \hat{\mathsf{F}}) + 2\mu] \phi_a(\boldsymbol{r}) \,.$$

Multiplying the whole expression by γ_0 from the left, we obtain the second-order Dirac equation,

$$\hat{\mathcal{H}} \phi_a(\boldsymbol{r}) = 0 \,, \quad \hat{\mathcal{H}} = \gamma_0 (\mathcal{E}_a - \hat{\mathsf{F}}) [\gamma_0 (\mathcal{E}_a - \hat{\mathsf{F}}) + 2\mu] \,, \tag{13}$$

where in the case of pure Coulomb potential, the second-order Dirac Hamiltonian $\hat{\mathcal{H}}$ is given by

$$\hat{\mathcal{H}} = \mathcal{E}_a^2 - \mu^2 - 2(\mu Z\alpha)^2 \left[\frac{\hat{\mathsf{p}}_r^2}{2} - \frac{\hat{\mathsf{G}}(\hat{\mathsf{G}} - 1)}{2\hat{\mathsf{r}}^2} - \frac{\mathcal{E}_a/\mu}{\hat{\mathsf{r}}} \right] , \tag{14}$$

where $\hat{\mathsf{p}}_r$ is radial momentum, in coordinate representation $\hat{\mathsf{p}}_r = -i \left(\frac{d}{dr} + \frac{1}{r} \right)$. The operator $\hat{\mathsf{G}}$ is the additional integral of motion for pure Coulomb potential

$$\hat{\mathsf{G}} = \gamma_0 \left(\hat{\mathsf{K}} + i (Z\alpha) \boldsymbol{\gamma} \cdot \boldsymbol{n} \right) , \tag{15}$$

where $\boldsymbol{n} = (\sin\vartheta \cos\varphi, \sin\vartheta \sin\varphi, \cos\vartheta)$ is the unit vector pointing in an arbitrary direction. The form (14) is up to the additive constant $\mathcal{E}_a^2 - \mu^2$ and up to the multiple of $-2(\mu Z\alpha)^2$ the same as the non-relativistic Hamiltonian with $\hat{\mathsf{G}}(\hat{\mathsf{G}} - 1)$ playing the role of the square of angular momentum $\hat{\mathsf{L}}^2$.

Simple calculation shows that

$$\hat{\mathsf{K}}^2 = \hat{\mathsf{J}}^2 + \frac{1}{4} \,, \quad \hat{\mathsf{G}}^2 = \hat{\mathsf{K}}^2 - (Z\alpha)^2 \,.$$

Whence the eigenvalues of the operators $\hat{\mathsf{K}}$ and $\hat{\mathsf{G}}$ read

$$K = \kappa |K| \,, \quad \kappa = \pm 1 \,, \quad |K| = j + 1/2 \tag{16}$$

and

$$G = g\kappa |G| \,, \quad g = \pm 1 \,, \quad |G| = \sqrt{K^2 - (Z\alpha)^2} \,, \tag{17}$$

respectively. Note that the sign of G is defined relative to the sign of K. In addition, it is worth noting that the operator $\hat{\mathsf{G}}$ is not Hermitian, but $\mathcal{PT}$-symmetric [17]

$$\hat{\mathsf{G}}^\dagger = \gamma_0 \hat{\mathsf{G}} \gamma_0 \,, \tag{18}$$

where † stands for Hermitian conjugation and γ_0 plays the role of the $\mathcal{P}$ (parity) operator.

All the operators $\hat{\mathsf{G}}, \hat{\mathsf{K}}, \hat{\mathsf{J}}^2$ and $\hat{\mathsf{J}}_z$ commute one with another; whence they possess common eigenfunctions

$$\begin{aligned} \hat{\mathsf{G}} |g, \kappa, j, m\rangle &= g\kappa |G| |g, \kappa, j, m\rangle \,, \\ \hat{\mathsf{K}} |g, \kappa, j, m\rangle &= \kappa |K| |g, \kappa, j, m\rangle \end{aligned} \tag{19}$$

and

$$\begin{aligned} \hat{\mathsf{J}}^2 |g, \kappa, j, m\rangle &= j(j+1) |g, \kappa, j, m\rangle \,, \\ \hat{\mathsf{J}}_z |g, \kappa, j, m\rangle &= m |g, \kappa, j, m\rangle . \end{aligned}$$

Their explicit from reads

$$\langle \boldsymbol{n} |\, g, \kappa, j, m\rangle = \begin{pmatrix} c_1^g \langle \boldsymbol{n} | j, m\rangle^{\kappa} \\ c_2^g \langle \boldsymbol{n} | j, m\rangle^{-\kappa} \end{pmatrix} , \tag{20}$$

where the symbol $\langle \boldsymbol{n} | j, m\rangle^{\kappa}$ denotes the spherical spinors

$$\langle \boldsymbol{n} |\, j, m\rangle^{\kappa} = \sum_{S_z = -\frac{1}{2}}^{\frac{1}{2}} \left(j - \frac{\kappa}{2}, m - S_z, \frac{1}{2}, S_z \middle| j, m \right) Y_{j - \frac{\kappa}{2}, m - S_z}(\boldsymbol{n}) \left| \frac{1}{2}, S_z \right\rangle . \tag{21}$$

Here $Y_{l,m}(\boldsymbol{n})$, $\left|\frac{1}{2}, S_z\right\rangle$ and $(|)$ are spherical harmonics, spin functions and Clebsch-Gordan coefficients, respectively, see any textbook on quantum mechanics, e.g. [19]. It follows from Eqs. (12), (15) and (19) that the coefficients c in the expansion (20) satisfy

$$c_2^g = -\frac{i}{Z\alpha} (K - G) c_1^g \,. \tag{22}$$

If this is supplemented with the normalization requirement

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where σ_i are 2-by-2 Pauli matrices and 1 and 0 are 2-by-2 identity and zero matrices, respectively. The fifth Dirac matrix, γ_5, which is needed later, see Eq. (94), has the explicit form

$$\gamma_5 = \begin{pmatrix} 0 & 1 \\ 1 & 0 \end{pmatrix} .$$

$$\langle g,\kappa,j,m|g,\kappa,j,m\rangle = |c_1^g|^2 + |c_2^g|^2 = 1\,, \tag{23}$$

the coefficients c are determined uniquely up to an overall phase. The explicit form of the coefficients c complying with Eqs. (22) and (23) is most easily obtained by introducing the angle θ by the relation

$$Z\alpha = |K|\sin\theta\,; \tag{24}$$

then, cf. Eq. (17),

$$|G| = |K|\cos\theta\,, \tag{25}$$

and, cf. Eqs. (20) and (22),

$$\langle \boldsymbol{n}|+,\kappa,j,m\rangle = \begin{pmatrix} \cos\frac{\theta}{2}\langle \boldsymbol{n}|j,m\rangle^{\kappa} \\ -i\kappa\sin\frac{\theta}{2}\langle \boldsymbol{n}|j,m\rangle^{-\kappa} \end{pmatrix} \tag{26}$$

and

$$\langle \boldsymbol{n}|-,\kappa,j,m\rangle = \begin{pmatrix} \sin\frac{\theta}{2}\langle \boldsymbol{n}|j,m\rangle^{\kappa} \\ -i\kappa\cos\frac{\theta}{2}\langle \boldsymbol{n}|j,m\rangle^{-\kappa} \end{pmatrix}. \tag{27}$$

2.3. Hydrogenic solution

To motivate our choice of the expansion of the eigenfuctions of the Fock operator (8), see Eqs. (36) and (38) below, we first show here the hydrogenic solution in the basis (26), (27). As it is clear from Eq. (14), the spinor-angular and radial degrees of freedom can be separated in the case of pure Coulomb potential

$$\phi_a(\boldsymbol{r}) = R_{n_A,l_g}(\xi_A,r)\langle \boldsymbol{n}|\,g,\kappa_A,j_A,m\rangle\,. \tag{28}$$

From Eqs. (14), (19) and the last equation we obtain equation for the radial hydrogenic functions

$$\begin{aligned}&\left[\frac{\hat{p}_r^2}{2} + \frac{l_g(l_g+1)}{2r^2} - \frac{\mathcal{E}_a/\mu}{r}\right] R_{n_A,l_g}(\xi_A,r) \\ &= \frac{\mathcal{E}_a^2-\mu^2}{2(\mu Z\alpha)^2} R_{n_A,l_g}(\xi_A,r)\,,\end{aligned} \tag{29}$$

where the effective angular quantum number l_g is determined from equation

$$l_g(l_g+1) = G(G-1)\,. \tag{30}$$

Requiring $l_g > -1$ so that the radial functions are normalizable, we obtain $l_g = |G|-1$ for $G>0$ and $l_g = |G|$ for $G<0$. In view of Eq. (19) this can be written concisely as

$$l_g = |G| - \delta_{g,\kappa_A}\,. \tag{31}$$

Substitution $r \to r/\xi_A$, where

$$\xi_A = \frac{\mathcal{E}_a}{\mu n_A}\,, \tag{32}$$

converts Eq. (29) into equation for Sturmian functions (see e.g. [16,19,20])

$$\begin{aligned}&\frac{1}{2}\left[r\hat{p}_r^2 + \frac{l(l+1)}{r} + r\right] R_{n,l}(r) = nR_{n,l}(r)\,, \\ &\quad n = k+l+1\,,\quad k = 0,1,2,\dots\,,\end{aligned} \tag{33}$$

where in the case considered clearly $l = l_g$, $n = n_A$ and

$$\mathcal{E}_a = \frac{\mu}{\sqrt{1+\left(\frac{Z\alpha}{n_A}\right)^2}}\,. \tag{34}$$

The screened Sturmian functions appearing in Eq. (29), which will be extensively used further in the paper, are related to the functions (33) by the relation

$$R_{n,l}(\xi,r) = \xi R_{n,l}(\xi r)\,, \tag{35}$$

where the multiplicative factor ξ ensures that the screened functions have the same normalization, see Eq. (B.3) below, as the functions (33).

2.4. Form of the spin-orbitals

The Fock operator (8) mixes states (28) with different signs of g and different principal quantum numbers n. Thus, a general eigenstate of the Fock operator (8) can be searched for in the form

$$\begin{aligned}\langle \boldsymbol{r}|\,a\rangle &= \langle \boldsymbol{r}|\,n_A,\kappa_A,j_A,m\rangle \\ &= \langle r|\,n_A,|G|-\delta_{\kappa_A,+}\rangle\langle \boldsymbol{n}|+,\kappa_A,j_A,m\rangle \\ &\quad + \langle r|\,n_A,|G|-\delta_{\kappa_A,-}\rangle\langle \boldsymbol{n}|-,\kappa_A,j_A,m\rangle\,,\end{aligned} \tag{36}$$

where, $|G| = \sqrt{(j_A+1/2)^2-(Z\alpha)^2}$, cf. Eqs. (16) and (17). Furthermore, the bispinors $\langle \boldsymbol{n}|\,g,\kappa_A,j_A,m\rangle$ are given by Eqs. (26), (27) and the radial parts of the orbitals are expanded into the Sturmian functions (33), (35)

$$\begin{aligned}\langle r|\,n_A,|G|-1\rangle &= \sum_{k=0}^{N} c_{A,k}^{+} R_{k,|G|-1}(\xi_A,r)\,, \\ \langle r|\,n_A,|G|\rangle &= \sum_{k=0}^{N-1} c_{A,k}^{-} R_{k,|G|}(\xi_A,r)\,.\end{aligned} \tag{37}$$

In terms of notation in Eq. (36) this can be written concisely as

$$\langle r|\,n_A,|G|-\delta_{\kappa_A,g}\rangle = \sum_{k=0}^{N-\delta_{\kappa_A,-g}} c_{A,k}^{\delta_{\kappa_A,g}-\delta_{\kappa_A,-g}} R_{k,|G|-\delta_{\kappa_A,g}} \tag{38}$$

Henceforth we change the notation to

$$R_{n=k+l+1,l}(\xi,r) \to R_{k,l}(\xi,r)\,; \tag{39}$$

we designate the Sturmian functions by their number of nodes k that are natural numbers (including zero) and not by their principal quantum number $n = l+1+k$, which is irrational, see Eqs. (17) and (31). We found this change of designation useful when deriving and programming the difference equations for the integrals from the Sturmian functions discussed further. Further, the screening constant in Eq. (38) is set to

$$\xi_A = \frac{1}{n_A} \tag{40}$$

where n_A is the non-relativistic principle quantum number of the pertinent shell. We found that taking the value (32) does not make any notable difference on the result, see also discussion in Section 9.

2.5. Roothaan form of DHF equations

Substituting now expansions (36) and (38) into the DHF equation (11) and projecting this equation onto the considered basis vectors, we obtain the Roothaan form of the DHF equations [25]

$$\begin{aligned}&\sum_k \begin{pmatrix} f_{ik}^{++} & f_{ik}^{+-} \\ f_{ik}^{-+} & f_{ik}^{--} \end{pmatrix} \begin{pmatrix} c_{A,k}^{\delta_{\kappa_A,+}-\delta_{\kappa_A,-}} \\ c_{A,k}^{\delta_{\kappa_A,-}-\delta_{\kappa_A,+}} \end{pmatrix} \\ &= \epsilon_a \sum_k \begin{pmatrix} S_{ik}^{++} & S_{ik}^{+-} \\ S_{ik}^{-+} & S_{ik}^{--} \end{pmatrix} \begin{pmatrix} c_{A,k}^{\delta_{\kappa_A,+}-\delta_{\kappa_A,-}} \\ c_{A,k}^{\delta_{\kappa_A,-}-\delta_{\kappa_A,+}} \end{pmatrix}\,,\end{aligned} \tag{41}$$

where

$$f_{ik}^{g,\overline{g}} = z_{ik}^{g,\overline{g}} + \frac{1}{Z} v_{ik}^{g,\overline{g}} . \tag{42}$$

The operators $\hat{z}$ and $\hat{v}$ are given by Eqs. (9) and (10), respectively. The pertinent matrix elements are defined below in Eqs. (43), (44) and (53). Their calculation is described in the next three sections.

3. One-particle matrix elements

The matrix elements of one-particle operator $\hat{z}$ and overlap matrix are defined as,

$$z_{ik}^{g,\overline{g}} = \int_0^\infty dr r^2 R_{i,l_g}(\xi, r) \langle g, \kappa, j, m | \hat{z} | \overline{g}, \kappa, j, m \rangle R_{k,l_{\overline{g}}}(\xi, r) \tag{43}$$

and

$$S_{ik}^{g,\overline{g}} = \langle g, \kappa, j, m | \ \overline{g}, \kappa, j, m \rangle \int_0^\infty dr r^2 R_{i,l_g}(\xi, r) R_{k,l_{\overline{g}}}(\xi, r) , \tag{44}$$

respectively. Recall that $l_g = |G| - \delta_{g,\kappa_A}$, see Eq. (31).

First we rewrite the kinetic term in the one-particle operator (9) successively as

$$\begin{aligned} \frac{1}{Z\alpha} \gamma_0 \boldsymbol{\gamma} \cdot \hat{\boldsymbol{p}} &= -\frac{i}{Z\alpha} \gamma_0 \boldsymbol{\gamma} \cdot \boldsymbol{n} \left(\frac{\partial}{\partial r} - \frac{\boldsymbol{\Sigma} \cdot \hat{\boldsymbol{L}}}{r} \right) \\ &= -\frac{i}{Z\alpha} \gamma_0 \boldsymbol{\gamma} \cdot \boldsymbol{n} \left(\frac{\partial}{\partial r} + \frac{1}{r} - \frac{\hat{\mathrm{G}} - iZ\alpha \gamma_0 \boldsymbol{\gamma} \cdot \boldsymbol{n}}{r} \right) \\ &= -\frac{i}{Z\alpha} \gamma_0 \boldsymbol{\gamma} \cdot \boldsymbol{n} \left(\frac{\partial}{\partial r} - \frac{\hat{\mathrm{G}} - 1}{r} \right) + \frac{1}{r} \\ &= -\frac{\hat{\mathrm{G}} - \gamma_0 \hat{\mathrm{K}}}{(Z\alpha)^2} \left(\frac{\partial}{\partial r} - \frac{\hat{\mathrm{G}} - 1}{r} \right) + \frac{1}{r} , \end{aligned} \tag{45}$$

where Eqs. (12) and (15) were used in the second and fourth equalities. The spinor-angular part of the one-particle operator (9) can thus be written solely in terms of the operators $\hat{\mathrm{G}}$, $\hat{\mathrm{K}}$ and γ_0

$$\hat{z} = -\frac{\hat{\mathrm{G}} - \gamma_0 \hat{\mathrm{K}}}{(Z\alpha)^2} \left(\frac{\partial}{\partial r} - \frac{\hat{\mathrm{G}} - 1}{r} \right) + \frac{\gamma_0 - 1}{(Z\alpha)^2} . \tag{46}$$

The integration of the spinor-angular degrees of freedom in Eqs. (43) and (44) is then reduced to the simple calculation

$$\langle g, \kappa, j, m | \gamma_0 | g, \kappa, j, m \rangle = g \cos\theta ,$$

$$\langle -g, \kappa, j, m | \gamma_0 | g, \kappa, j, m \rangle = 0 ,$$

$$\langle g, \kappa, j, m | \ g, \kappa, j, m \rangle = 1 , \quad \langle -g, \kappa, j, m | \ g, \kappa, j, m \rangle = \sin\theta$$

and

$$\langle g, \kappa, j, m | (\hat{\mathrm{G}} - \gamma_0 \hat{\mathrm{K}}) | g, \kappa, j, m \rangle = 0 ,$$

$$\langle -g, \kappa, j, m | (\hat{\mathrm{G}} - \gamma_0 \hat{\mathrm{K}}) | g, \kappa, j, m \rangle = G \sin\theta ,$$

following from Eqs. (19)–(27). Substituting these results and Eq. (46) into Eq. (43) we get

$$\langle g, \kappa, j, m | \hat{z} | g, \kappa, j, m \rangle = \frac{g \cos\theta - 1}{(Z\alpha)^2} \tag{47}$$

and

$$\langle -g, \kappa, j, m | \hat{z} | g, \kappa, j, m \rangle = -\frac{\sin\theta}{(Z\alpha)^2} \left[1 + G \left(\frac{d}{dr} - \frac{G - 1}{r} \right) \right] . \tag{48}$$

To calculate the action of the last operator on the Sturmian functions, we recall that in [16] a number of recursive relations for Sturmian functions was derived; in particular, relations connecting functions with the same principal quantum number n and different orbital quantum number l: (note that here we temporarily label the Sturmian functions according to their principal quantum number n to make the point clear):

$$\begin{aligned} &\left(\frac{d}{dr} + \frac{l + 1}{r} \right) R_{n,l}(\xi, r) \\ &\quad = \frac{\xi}{l} \left[n R_{n,l}(\xi, r) + \sqrt{n^2 - l^2} R_{n,l-1}(\xi, r) \right] \end{aligned} \tag{49}$$

and

$$\begin{aligned} &\left(\frac{d}{dr} - \frac{l}{r} \right) R_{n,l}(\xi, r) \\ &\quad = -\frac{\xi}{l + 1} \left[n R_{n,l}(\xi, r) + \sqrt{n^2 - (l + 1)^2} R_{n,l+1}(\xi, r) \right] , \end{aligned} \tag{50}$$

see Eqs. (33) and (34) in [16] where the substitution $r \to r\xi$ is made. Note that there is a missing minus sign on the rhs of Eq. (34) in the cited paper.

The last two equations can be united into the single equation

$$\begin{aligned} &\left(\frac{d}{dr} - \frac{G - 1}{r} \right) R_{n,|G|-\delta_{g,\kappa}}(\xi, r) \\ &\quad = -\frac{\xi}{G} \left[n R_{n,|G|-\delta_{g,\kappa}}(\xi, r) + \sqrt{n^2 - G^2} R_{n,|G|-\delta_{-g,\kappa}}(\xi, r) \right] . \end{aligned} \tag{51}$$

Recalling that $G = g\kappa |G|$, see Eq. (17), Eqs. (49) and (50) then correspond to the cases $g = \kappa$, $|G| = l + 1$ and $g = -\kappa$, $|G| = l$ respectively. Thus, by means of Eq. (51) the calculation of the matrix elements (43) is completely reduced to calculation of the overlap integrals (44). Calculation of these integrals is outlined in Section 5.4.

4. Spinor-angular part of the two-electron interaction

To separate the angular and radial degrees of freedom in the matrix elements of the operator $\hat{v}$, Eq. (10), we expand r_{12}^{-1} in the multipole expansion

$$r_{12}^{-1} = \frac{1}{r_>} \sum_{l=0}^{\infty} \left(\frac{r_<}{r_>} \right)^l \frac{4\pi}{2l + 1} \sum_{m=-l}^{l} Y_{l,m}(\boldsymbol{n}_1) Y_{l,m}^*(\boldsymbol{n}_2) \tag{52}$$

where $r_< = r_1$, $r_> = r_2$ if $r_1 < r_2$ and $r_< = r_2$, $r_> = r_1$ if $r_1 > r_2$. Recall that $Y_{l,m}(\boldsymbol{n})$ stands for spherical harmonics.

The matrix elements of $\hat{v}$ in Eq. (42) are given as

$$\begin{aligned} v_{ik}^{g,\overline{g}} = &\sum_{\{n_B, j_B, \kappa_B\}} \sum_{p,g'} \sum_{q,\overline{g}'} c_{B,p}^{\delta_{\kappa_B,g'} - \delta_{\kappa_B,-g'}} c_{B,q}^{\delta_{\kappa_B,\overline{g}'} - \delta_{\kappa_B,-\overline{g}'}} \\ &\sum_{l=0}^{\infty} \mathcal{A}^C(j_A, \kappa_A, g, \overline{g}, j_B, \kappa_B, g', \overline{g}', l) \\ &\quad \times \mathcal{R}(\{i, l_g, \xi_A\}, \{p, l_{g'}, \xi_B\}, \{k, l_{\overline{g}}, \xi_A\}, \{q, l_{\overline{g}'}, \xi_B\}, l) \\ &\quad - \mathcal{A}^E(j_A, \kappa_A, g, \overline{g}, j_B, \kappa_B, g', \overline{g}', l) \\ &\quad \times \mathcal{R}(i, l_g, \xi_A\}, \{p, l_{g'}, \xi_B\}, \{q, l_{\overline{g}'}, \xi_B\}, \{k, l_{\overline{g}}, \xi_A\}, l) \end{aligned} \tag{53}$$

where the spinor-angular part of the Coulomb and exchange integrals reads

$$
\begin{aligned}
&\mathcal{A}^C(j_A, \kappa_A, g, \overline{g}, j_B, \kappa_B, g', \overline{g}', l) \\
&= \frac{4\pi}{2l+1} \sum_{m=-l}^{l} \sum_{m_B=-j_B}^{j_B} \langle g, \kappa_A, j_A, m_A | Y_{l,m}(\hat{\boldsymbol{n}}) | \overline{g}, \kappa_A, j_A, m_A \rangle \\
&\quad \times \langle g', \kappa_B, j_B, m_B | Y^*_{l,m}(\hat{\boldsymbol{n}}) | \overline{g}', \kappa_B, j_B, m_B \rangle ,
\end{aligned} \tag{54}
$$

and

$$
\begin{aligned}
&\mathcal{A}^E(j_A, \kappa_A, g, \overline{g}, j_B, \kappa_B, g', \overline{g}', l) \\
&= \frac{4\pi}{2l+1} \sum_{m=-l}^{l} \sum_{m_B=-j_B}^{j_B} \langle g, \kappa_A, j_A, m_A | Y_{l,m}(\hat{\boldsymbol{n}}) | \overline{g}', \kappa_B, j_B, m_B \rangle \\
&\quad \times \langle g', \kappa_B, j_B, m_B | Y^*_{l,m}(\hat{\boldsymbol{n}}) | \overline{g}, \kappa_A, j_A, m_A \rangle ,
\end{aligned} \tag{55}
$$

respectively and radial part of the integrals, $\mathcal{R}$, is defined below, Eq. (58). Clearly, the calculation of these matrix elements involves calculation of the matrix elements of spherical harmonics between the bispinors (20)

$$
\begin{aligned}
&\langle g, \kappa_A, j_A, m_A | Y_{l,m}(\hat{\boldsymbol{n}}) | g', \kappa_B, j_B, m_B \rangle \\
&= (c_1^g)^* c_1^{g'} \langle j_A, m_A |^{\kappa_A} Y_{l,m}(\hat{\boldsymbol{n}}) | j_B, m_B \rangle^{\kappa_B} \\
&\quad + (c_2^g)^* c_2^{g'} \langle j_A, m_A |^{-\kappa_A} Y_{l,m}(\hat{\boldsymbol{n}}) | j_B, m_B \rangle^{-\kappa_B} .
\end{aligned} \tag{56}
$$

Using further the definition of spherical spinors (21), the orthonormality of the spin vectors and the Wigner-Eckart theorem for angular integration, we obtain for the matrix elements of spherical harmonics between spherical spinors

$$
\begin{aligned}
&\langle j_A, m_A |^{\kappa_A} Y_{l,m}(\hat{\boldsymbol{n}}) | j_B, m_B \rangle^{\kappa_B} \\
&= \delta_{m, m_A - m_B} \left(j_A - \frac{\kappa_A}{2}, 0, j_B - \frac{\kappa_B}{2}, 0 | l, 0 \right) \\
&\quad \times \sqrt{\frac{(2j_A + 1 - \kappa_A)(2j_B + 1 - \kappa_B)}{(2l+1)4\pi}} \\
&\quad \times \sum_{S_z = -\frac{1}{2}}^{\frac{1}{2}} \left(j_A - \frac{\kappa_A}{2}, m_A - S_z, \frac{1}{2}, S_z | j_A, m_A \right) \\
&\quad \times \left(j_B - \frac{\kappa_B}{2}, m_B - S_z, \frac{1}{2}, S_z | j_B, m_B \right) (-1)^{2m_A - m_B - S_z} \\
&\quad \times \left(j_A - \frac{\kappa_A}{2}, -m_A + S_z, j_B - \frac{\kappa_B}{2}, m_B - S_z | l, -m \right) .
\end{aligned} \tag{57}
$$

It follows from the selection rules for Clebsch-Gordan coefficients that the rhs of the last equation vanishes unless $|j_A - j_B - \frac{\kappa_A - \kappa_B}{2}| \le l \le j_A + j_B - \frac{\kappa_A + \kappa_B}{2}$ and $l + j_A - j_B - \frac{\kappa_A + \kappa_B}{2}$ is an even number. For the second term on the rhs of Eq. (56) we obtain the same rules simply by replacing $\kappa_{A,B}$ by $-\kappa_{A,B}$. Whence, the infinite sum over multipoles l in Eq. (53) collapses to only a few terms.

The last equation is substituted into the next to the last equation, Eq. (56). This equation is then substituted into Eqs. (54) and (55). The resulting sums can be performed either elegantly by means of a high level angular momentum theory, see e.g. [26,27], or by brute force computer computation. The net result is that $\mathcal{A}^C$ vanishes unless $l = 0$.

5. Radial part of the two-electron interaction

The radial part of the integration in Eq. (53) involves calculation of the integrals

$$
\begin{aligned}
&\mathcal{R}(\{i, l_1, \xi_1\}, \{p, l_2, \xi_2\}, \{k, l_3, \xi_3\}, \{q, l_4, \xi_4\}, l) \\
&= \int_0^\infty dr_1 R_{i,l_1}(\xi_1, r_1) R_{k,l_3}(\xi_3, r_1) r_1^{l+2} \\
&\quad \times \int_{r_1}^\infty dr_2 R_{p,l_2}(\xi_2, r_2) R_{q,l_4}(\xi_4, r_2) r_2^{-l+1} \\
&\quad + \int_0^\infty dr_1 R_{i,l_1}(\xi_1, r_1) R_{k,l_3}(\xi_3, r_1) r_1^{-l+1} \\
&\quad \times \int_0^{r_1} dr_2 R_{p,l_2}(\xi_2, r_2) R_{q,l_4}(\xi_4, r_2) r_2^{l+2} .
\end{aligned} \tag{58}
$$

5.1. Linearization of the product of two functions

Following [16] we first write the product of radial functions of the same variable as a linear combination of radial functions, Eq. (49) of [16],

$$
\begin{aligned}
&r^p R_{k_1,l_1}(\xi_1, r) R_{k_2,l_2}(\xi_2, r) \\
&= \sum_{k=0}^{k_1+k_2+p} (k_1, l_1, \xi_1, k_2, l_2, \xi_2 | k)_p R_{k, l_1+l_2}(\xi_1 + \xi_2, r) .
\end{aligned} \tag{59}
$$

For the coefficients of the linear combination the following difference equation holds, see Eq. (53) of [16],

$$
\begin{aligned}
&(k_1, l_1, \xi_1, k_2, l_2, \xi_2 | k)_p \sqrt{k_1(k_1 + 2l_1 + 1)} \\
&= 2\left(k_1 + l_1 - \frac{\xi_1(k + l_1 + l_2 + 1)}{\xi_1 + \xi_2} \right) \\
&\quad \times (k_1 - 1, l_1, \xi_1, k_2, l_2, \xi_2 | k)_p \\
&\quad - \sqrt{(k_1 + 2l_1)(k_1 - 1)} (k_1 - 2, l_1, \xi_1, k_2, l_2, \xi_2 | k)_p \\
&\quad + \frac{\xi_1}{\xi_1 + \xi_2} \sqrt{(k + 2(l_1 + l_2) + 1)k} (k_1 - 1, l_1, \xi_1, k_2, l_2, \\
&\quad \xi_2 | k - 1)_p + \frac{\xi_1}{\xi_1 + \xi_2} \sqrt{(k+1)(k + 2(l_1 + l_2) + 2)} \\
&\quad \times (k_1 - 1, l_1, \xi_1, k_2, l_2, \xi_2 | k + 1)_p .
\end{aligned} \tag{60}
$$

It turns out that this equation becomes numerically unstable for large numbers of nodes (of the order of forty) when $k_2 > k_1$. Thus, in order to achieve high numerical stability this equation is used for $k_1 \ge k_2$. For $k_2 > k_1$ we use the same equation, but with the roles of 1 and 2 swapped:

$$
\begin{aligned}
&(k_1, l_1, \xi_1, k_2, l_2, \xi_2 | k)_p \sqrt{k_2(k_2 + 2l_2 + 1)} \\
&= 2\left(k_2 + l_2 - \frac{\xi_2(k + l_1 + l_2 + 1)}{\xi_1 + \xi_2} \right) \\
&\quad \times (k_1, l_1, \xi_1, k_2 - 1, l_2, \xi_2 | k)_p \\
&\quad - \sqrt{(k_2 + 2l_2)(k_2 - 1)} (k_1, l_1, \xi_1, k_2 - 2, l_2, \xi_2 | k)_p \\
&\quad + \frac{\xi_2}{\xi_1 + \xi_2} \sqrt{(k + 2(l_1 + l_2) + 1)k} \\
&\quad \times (k_1, l_1, \xi_1, k_2 - 1, l_2, \xi_2 | k - 1)_p \\
&\quad + \frac{\xi_2}{\xi_1 + \xi_2} \sqrt{(k+1)(k + 2(l_1 + l_2) + 2)} \\
&\quad \times (k_1, l_1, \xi_1, k_2 - 1, l_2, \xi_2 | k + 1)_p .
\end{aligned} \tag{61}
$$

For the case of interest, $p = 1$, the equation (60) is solved with the initial conditions, see Eqs. (56)–(58) in [16],

$$
\begin{aligned}
&(0, l_1, \xi_1, 0, l_2, \xi_2|0)_1 \\
&\quad = 2(l_1+l_2+1)\frac{\xi_1^{l_1+1}\xi_2^{l_2+1}}{(\xi_1+\xi_2)^{l_1+l_2+2}}\sqrt{\frac{(2l_1+2l_2+1)!}{(2l_1+1)!(2l_2+1)!}}\,,
\end{aligned}
\tag{62}
$$

$$
\begin{aligned}
&(0, l_1, \xi_1, 0, l_2, \xi_2|1)_1 \\
&\quad = -\sqrt{2(l_1+l_2+1)}\frac{\xi_1^{l_1+1}\xi_2^{l_2+1}}{(\xi_1+\xi_2)^{l_1+l_2+2}}\sqrt{\frac{(2l_1+2l_2+1)!}{(2l_1+1)!(2l_2+1)!}}
\end{aligned}
\tag{63}
$$

and

$$
(k_1, l_1, \xi_1, k_2, l_2, \xi_2|k)_1 = 0\,, \quad k > k_1+k_2+1\,, \quad k < 0\,. \tag{64}
$$

Using Eq. (59) for $p = 1$, the integrals (58) can be written as

$$
\begin{aligned}
&\mathcal{R}(\{i, l_1, \xi_1\}, \{p, l_2, \xi_2\}, \{k, l_3, \xi_3\}, \{q, l_4, \xi_4\}, l) \\
&= \sum_{u,v}(i, l_1, \xi_1, k, l_3, \xi_3|u)_1(p, l_2, \xi_2, q, l_4, \xi_4|v)_1 \\
&\times\Big[P^{l_1+l_3,l_2+l_4,l}_{u,v}(\xi_1+\xi_3, \xi_2+\xi_4) + P^{l_2+l_4,l_1+l_3,l}_{v,u}(\xi_2+\xi_4, \xi_1+\xi_3)\Big] \\
&\times\sqrt{\frac{u!}{(u+2\,(l_1+l_3)+1)!}}\sqrt{\frac{v!}{(v+2\,(l_2+l_4)+1)!}}\,,
\end{aligned}
\tag{65}
$$

where

$$
\begin{aligned}
&P^{L_1,L_2,l}_{k_1,k_2}(\xi_1, \xi_2) \\
&= \int_0^\infty \tilde{R}_{k_1,L_1}(\xi_1 r_1) r_1^{l+1}\int_{r_1}^\infty \tilde{R}_{k_2,L_2}(\xi_2 r_2) r_2^{-l}\, dr_2\, dr_1
\end{aligned}
\tag{66}
$$

and

$$
\begin{aligned}
&P^{L_2,L_1,l}_{k_2,k_1}(\xi_2, \xi_1) \\
&= \int_0^\infty \tilde{R}_{k_1,L_1}(\xi_1 r_1) r_1^{-l}\int_0^{r_1} \tilde{R}_{k_2,L_2}(\xi_2 r_2) r_2^{l+1}\, dr_2\, dr_1\,.
\end{aligned}
\tag{67}
$$

The unnormalized radial functions $\tilde{R}_{k,l}(r)$ are related to the normalized functions $R_{k,l}(r)$ via relation

$$
\tilde{R}_{k,l}(r) = \sqrt{\frac{(k+2l+1)!}{k!}}R_{k,l}(r). \tag{68}
$$

By using the unnormalized functions, the irrational factors are conveniently eliminated.

5.2. Difference equations for the integrals $P^{L_1,L_2,l}_{k_1,k_2}(\xi_1, \xi_2)$

For the integrals (66) a number of difference equations was derived in [16]. In particular, the following relations that lower the number of nodes of the radial functions k_2 and k_1, while other quantum numbers are fixed, hold, see Eqs. (67) and (72) of [16],

$$
\begin{aligned}
&(k_2+1)P^{L_1,L_2,l}_{k_1,k_2+1}(\xi_1, \xi_2) - 2lP^{L_1,L_2,l}_{k_1,k_2}(\xi_1, \xi_2) \\
&\quad - (k_2+2L_2+1)P^{L_1,L_2,l}_{k_1,k_2-1}(\xi_1, \xi_2) \\
&= -2(k_1, L_1, \xi_1|r|k_2, L_2, \xi_2)
\end{aligned}
\tag{69}
$$

and

$$
\begin{aligned}
&(k_1+1)P^{L_1,L_2,l}_{k_1+1,k_2}(\xi_1, \xi_2) + 2(l+1)P^{L_1,L_2,l}_{k_1,k_2}(\xi_1, \xi_2) \\
&\quad - (k_1+2L_1+1)P^{L_1,L_2,l}_{k_1-1,k_2}(\xi_1, \xi_2) = 2(k_1, L_1, \xi_1|r|k_2, L_2, \xi_2)\,,
\end{aligned}
\tag{70}
$$

respectively. Here, the one-particle radial integrals on the rhs of these equations are defined as

$$
(k_1, L_1, \xi_1|r|k_2, L_2, \xi_2) = \int_0^\infty r^2\tilde{R}_{k_1,L_1}(\xi_1, r)\tilde{R}_{k_2,L_2}(\xi_2, r)\, dr. \tag{71}
$$

Relations (69) and (70) reduce the integrals (66) to the integrals over nodeless functions $P^{L_1,L_2,l}_{0,0}(\xi_1, \xi_2)$. These integrals can be in turn expressed for general non-integer values of orbital quantum numbers L_1 and L_2 in terms of the hypergeometric function as

$$
\begin{aligned}
P^{L_1,L_2,l}_{0,0}(\xi_1, \xi_2) &= \frac{2^{L_1+L_2+2}\xi_1^{L_1+1}\xi_2^{-L_1-2}\Gamma(L_1+L_2+3)}{l+L_1+2} \\
&\times F\left(L_1+l+2, L_1+L_2+3, L_1+l+3, -\frac{\xi_1}{\xi_2}\right).
\end{aligned}
\tag{72}
$$

The method for calculation of this particular type of the hypergeometric function is given in Appendix A.

In the case when the difference of the orbital quantum numbers $L_2 - L_1$ is an integer, and only if there is such a case, it is advantageous to lower the orbital quantum number L_2 to the value L_1 or L_1 to L_2 by means of the relations, see Eqs. (75) or (81) in [16],

$$
\begin{aligned}
&-2lP^{L_1,L_2+1,l}_{k_1,k_2-1}(\xi_1, \xi_2) - 2(L_2+1)P^{L_1,L_2+1,l}_{k_1,k_2}(\xi_1, \xi_2) \\
&\quad + 2(L_2+1-l)(k_2+2L_2+2)P^{L_1,L_2,l}_{k_1,k_2}(\xi_1, \xi_2) \\
&= -\frac{2(L_2+1)}{\xi_2}\,[(k_1, L_1, \xi_1|k_2, L_2+1, \xi_2) \\
&\quad -(k_1, L_1, \xi_1|k_2-1, L_2+1, \xi_2)]\,,
\end{aligned}
\tag{73}
$$

and

$$
\begin{aligned}
&-2(L_1+1)P^{L_1+1,L_2,l}_{k_1,k_2}(\xi_1, \xi_2) + 2(l+1)P^{L_1+1,L_2,l}_{k_1-1,k_2}(\xi_1, \xi_2) \\
&\quad + 2(L_1+l+2)(k_1+2L_1+2)P^{L_1,L_2,l}_{k_1,k_2}(\xi_1, \xi_2) \\
&= \frac{2(L_1+1)}{\xi_1}\Big[(k_1, L_1+1, \xi_1|k_2, L_2, \xi_2) \\
&\quad - (k_1-1, L_1+1, \xi_1|k_2, L_2, \xi_2)\Big],
\end{aligned}
\tag{74}
$$

respectively. The one-particle integrals on the rhs of the last two equations are defined as, cf. Eq. (71),

$$
(k_1, L_1, \xi_1|k_2, L_2, \xi_2) = \int_0^\infty r\tilde{R}_{k_1,L_1}(\xi_1, r)\tilde{R}_{k_2,L_2}(\xi_2, r)\, dr. \tag{75}
$$

In contrast to the non-relativistic case, it can happen here that spinor-angular integration does not enforce that both L_1 and L_2 have to be greater than the order l of the multipole expansion. In such a case, it is still advantageous to use Eq. (73) if $L_2 > L_1$. However, in the case when $L_1 > L_2$, it is not advantageous to decrease further the value of L_1 by means of Eq. (74), but instead to increase the value of L_2 by means of Eq. (73).

5.3. Asymptotic solution of difference equations

As follows from Eqs. (53) and (65), when we calculate the exchange integrals we always calculate the integrals (66) for the case $\xi_1 = \xi_2$ and $|L_1 - L_2| = 0, 1, 2$. As already observed in [28] in the non-relativistic setting, in such a case the calculation of the integrals (66) through the direct use of difference equations (69) and (70) does not yield numerically stable results for the integrals involving a large number of nodes k_1, k_2. In [16] and [28] numerically stable ways of calculation of the integrals (66) were suggested. However, both these procedures work only in the non-relativistic setting. Here we come yet with another solution that works also in the relativistic case. It can be used in the non-relativistic case, too, cf. [22].

In the case when $|L_1 - L_2| = 1, 2$, we use Eqs. (73) and (74) in the way just described. We thus always reduce the calculation of the exchange integrals to the calculation of integrals (66), where $\xi_1 = \xi_2$ and $L_1 = L_2$. In such a case the one-particle integrals on the rhs of Eqs. (69) and (70) are zero for $|k_2 - k_1| > 1$, see Eqs. (82) and (88) below. Thus, for $k_2 \neq k_1$ it suffices to solve homogeneous equations (69) and (70).

Both linearly independent solutions of homogeneous Eqs. (69) and (70) can be obtained as a solution of the equation

$$(k+1)[a_{k+1,p,L} - a_{k-1,p,L}] - 2La_{k-1,p,L} + 2pa_{k,p,L} = 0\,. \tag{76}$$

The two linearly independent solutions of homogeneous Eq. (69) are obtained by setting $P^{L_1,L_2,l}_{k_1,k_2}(\xi_1,\xi_2) = a_{k_2,-l,L_2}$ and $P^{L_1,L_2,l}_{k_1,k_2}(\xi_1,\xi_2) = (-1)^{k_2} a_{k_2,l,L_2}$. Likewise, the two linearly independent solutions of homogeneous Eq. (70) are obtained by setting $P^{L_1,L_2,l}_{k_1,k_2}(\xi_1,\xi_2) = a_{k_1,l+1,L_1}$ and $P^{L_1,L_2,l}_{k_1,k_2}(\xi_1,\xi_2) = (-1)^{k_1} a_{k_1,-l-1,L_1}$.

Following the general method outlined in [29], we search for an asymptotic solution of Eq. (76) in the form

$$a_{k,p,L} = \sum_{q=0}^{Q} A_q \frac{\Gamma(k)}{\Gamma(k+q-L+p)}\,. \tag{77}$$

In actual calculation we take $Q \simeq 25$. Substituting this into Eq. (76) we obtain after some algebraic manipulation recursive relation for coefficients A_q

$$\begin{aligned} &A_{q+1}(-2)(q+1) + A_q(q-L+p)(3q-3-3L+p) \\ &\quad - A_{q-1}(q-L+p)(q-L+p-1)(q-L+p-2) = 0\,. \end{aligned} \tag{78}$$

One starts this recurrence with $q = 0$ setting $A_{-1} = 0$; A_0 is an overall multiplicative constant undetermined from these relations, but all A_q/A_0 for $q > 0$ are determined uniquely. We set $A_0 = 1$ and determine overall multiplicative constant as described below.

For $|k_1 - k_2| > 0$ general solution of Eqs. (69) and (70) for the case $L_1 = L_2 = L$ and $\xi_1 = \xi_2 = \xi$ can be written in the form

$$\begin{aligned} &P^{L,L,l}_{k_1,k_2}(\xi,\xi) = [c_{1,1}a_{k_1,l+1,L} + c_{1,2}a_{k_1,-l-1}(-1)^{k_1}]a_{k_2,-l,L} \\ &\quad + [c_{2,1}a_{k_1,l+1,L} + c_{2,2}a_{k_1,-l-1,L}(-1)^{k_1}]a_{k_2,l,L}(-1)^{k_2}\,, \\ &|k_1 - k_2| > 0\,, \quad k_{1,2} \geq k_0\,, \end{aligned} \tag{79}$$

where $k_0 \simeq 10$ is the smallest number for which the asymptotic solution (77) holds to desired accuracy; further,

$$P^{L,L,l}_{k_1,k_2}(\xi,\xi) = c_{1,1}a_{k_1,l+1} + c_{1,2}a_{k_1,-l-1}(-1)^{k_1} \quad k_1 \geq k_0 > k_2 \tag{80}$$

and

$$P^{L,L,l}_{k_1,k_2}(\xi,\xi) = c_{1,1}a_{k_2,-l} + c_{2,1}a_{k_2,l}(-1)^{k_2} \quad k_2 \geq k_0 > k_1\,. \tag{81}$$

The coefficients c are fitted to the actual values of the integrals obtained by running equations (69) and (70) up to $k_{1,2} \simeq 10$. As already observed in [28] in the non-relativistic setting, additional simplifications appear; they must be taken into account for a numerically stable determination of coefficients c in Eqs. (79)–(81).

1. If $k_2 > k_1 \geq k_0$ then $c_{1,1} = c_{1,2} = 0$ and $c_{2,2} = \frac{2}{\xi}$; the coefficient $c_{2,1}$ is obtained by fitting (79) on the value $P^{L,L,l}_{k_0,k_0+1}(\xi,\xi)$.
2. If $k_1 > k_2 \geq k_0$ and $l > 0$ then $c_{1,2} = c_{2,2} = 0$; the coefficients $c_{1,1}$ and $c_{2,1}$ are obtained by fitting (79) on the values $P^{L,L,l}_{k_0+1,k_0}(\xi,\xi)$ and $P^{L,L,l}_{k_0+2,k_0+1}(\xi,\xi)$.
3. If $k_1 > k_2 \geq k_0$, $l = 0$ and $k_2 \mod 2 = 0$ then $c_{1,2} = c_{2,2} = 0$ and $c_{2,1} = c_{1,1}$; the coefficient $c_{1,1}$ is obtained by fitting (79) on the value $P^{L,L,0}_{k_0+1,k_0}(\xi,\xi)$.
4. If $k_1 > k_2$, $l = 0$ and $k_2 \mod 2 = 1$ then $P^{L,L,0}_{k_1,k_2}(\xi,\xi) = 0$.
5. If $k_1 \geq k_0 > k_2$ then $c_{1,2} = 0$; the coefficient $c_{1,1}$ is obtained by fitting (80) on the value $P^{L,L,l}_{k_0,k_2}(\xi,\xi)$.
6. If $k_2 \geq k_0 > k_1$ then $c_{1,1} = 0$; the coefficient $c_{2,1}$ is obtained by fitting (81) on the value $P^{L,L,l}_{k_1,k_0}(\xi,\xi)$.

As mentioned in Section 4, the spinor-angular integration reduces the calculation of the Coulomb integrals to the case $l = 0$ only. If $\xi_1 = \xi_2$ and $L_1 = L_2$, the integrals (66) are calculated as described above. If this is not the case, the integrals (66) can be calculated directly, in a numerically stable way, from the relations (69) and (70). The difficult part is then the calculation of the one-particle integrals on the rhs of these equations, to which we turn next.

5.4. One-particle integrals

Calculation of the overlap integrals (71), appearing in Eqs. (43), (69) and (70), is by means of relation, see Eq. (78) of [16],

$$\begin{aligned} &2\xi_2(k_1, L_1, \xi_1|r^p|k_2, L_2, \xi_2) \\ &\quad = 2(k_2 + L_2 + 1)(k_1, L_1, \xi_1|r^{p-1}|k_2, L_2, \xi_2) \\ &\quad\quad - (k_2 + 1)(k_1, L_1, \xi_1|r^{p-1}|k_2 + 1, L_2, \xi_2) \\ &\quad\quad - (k_2 + 2L_2 + 1)(k_1, L_1, \xi_1|r^{p-1}|k_2 - 1, L_2, \xi_2) \end{aligned} \tag{82}$$

reduced to the calculation of the overlap integrals (75). To calculate these integrals we have to again distinguish whether the difference $L_1 - L_2$ is an integer or not.

If the difference $L_1 - L_2$ is not an integer, integrals (75) are calculated by means of the difference equations, see Eq. (B7) of [16],

$$\begin{aligned} &(k_2 + 1)\left(\frac{1}{\xi_1} + \frac{1}{\xi_2}\right)(k_1, L_1, \xi_1|k_2 + 1, L_2, \xi_2) \\ &\quad = 2\left(-\frac{k_1 + L_1 + 1}{\xi_1} + \frac{k_2 + L_2 + 1}{\xi_2}\right)(k_1, L_1, \xi_1|k_2, L_2, \xi_2 \\ &\quad\quad + (k_2 + 2L_2 + 1)\left(\frac{1}{\xi_1} - \frac{1}{\xi_2}\right)(k_1, L_1, \xi_1|k_2 - 1, L_2, \xi_2) \\ &\quad\quad + 2\frac{k_1 + 2L_1 + 1}{\xi_1}(k_1 - 1, L_1, \xi_1|k_2, L_2, \xi_2)\,. \end{aligned} \tag{83}$$

This equation is used when $\xi_1 \geq \xi_2$ and $k_1 \leq k_2 + s$. The number s was determined on basis of numerical experiments as follows. If $L_1 > L_2$ then $s = \min\left\{10\left(\frac{2}{\xi_2} - \frac{2}{\xi_1} - 1\right), 23\right\}$; if $L_2 \geq L_1$ and $\xi_1 < 2$ then $s = 18\left(\frac{1}{\xi_2} - \frac{1}{\xi_1}\right)$; for $\xi_1 = 2$ $s = 5\left(\frac{2}{\xi_2} - \frac{2}{\xi_1} + 3\right)$. If k_2 reaches zero, we swap the roles of 1 and 2 in Eq. (83):

$$\begin{aligned} &(k_1 + 1)\left(\frac{1}{\xi_1} + \frac{1}{\xi_2}\right)(k_1 + 1, L_1, \xi_1|k_2 + 1, L_2, \xi_2) \\ &\quad = 2\left(\frac{k_1 + L_1 + 1}{\xi_1} - \frac{k_2 + L_2 + 1}{\xi_2}\right)(k_1, L_1, \xi_1|k_2, L_2, \xi_2) \\ &\quad\quad + (k_1 + 2L_1 + 1)\left(-\frac{1}{\xi_1} + \frac{1}{\xi_2}\right)(k_1 - 1, L_1, \xi_1|k_2, L_2, \xi_2) \\ &\quad\quad + 2\frac{k_2 + 2L_2 + 1}{\xi_2}(k_1, L_1, \xi_1|k_2 - 1, L_2, \xi_2)\,. \end{aligned} \tag{84}$$

If both k_1 and k_2 are zero then

$$(0, l_1, \xi_1 | 0, l_2, \xi_2) = (2\xi_1)^{L_1+1} (2\xi_2)^{L_2+1} \frac{\Gamma(L_1+L_2+2)}{(\xi_1+\xi_2)^{L_1+L_2+2}} . \tag{85}$$

If $\xi_1 \geq \xi_2$ and $k_1 > k_2 + s$, we use Eq. (84) unless $k_1 \leq k_2 + s$; then we use Eq. (83). If $\xi_1 < \xi_2$, we use an obvious relation

$$(k_1, L_1, \xi_1 | k_2, L_2, \xi_2) = (k_2, L_2, \xi_2 | k_1, L_1, \xi_1) . \tag{86}$$

If the difference $L_2 - L_1$ is an integer, then if $L_2 > L_1$ we use Eq. (B10) of [16]

$$\begin{aligned} & 2(k_1 + L_1 + L_2 + 2)(k_1, L_1, \xi_1 | k_2, L_2, \xi_2) \\ & \quad = 2(k_1 + 2L_1 + 1)(k_1 - 1, L_1, \xi_1 | k_2, L_2, \xi_2) - \left(1 - \frac{\xi_1}{\xi_2}\right) \\ & \qquad \times (k_1, L_1, \xi_1 | k_2 - 2, L_2 + 1, \xi_2) \\ & \qquad - 2\frac{\xi_1}{\xi_2}(k_1, L_1, \xi_1 | k_2 - 1, L_2 + 1, \xi_2) + \left(1 + \frac{\xi_1}{\xi_2}\right) \\ & \qquad \times (k_1, L_1, \xi_1 | k_2, L_2 + 1, \xi_2) . \end{aligned} \tag{87}$$

If $L_1 > L_2$ we use first Eq. (86) to swap the roles of 1 and 2 and then use Eq. (87). If $L_1 = L_2$ then we proceed as follows. If $\xi_1 = \xi_2$ then, see Eqs. (68) and (B.3) below,

$$(k_1, L, \xi | k_2, L, \xi) = \delta_{k_1, k_2} \frac{(k_1 + 2L + 1)!}{k_1!} ; \tag{88}$$

otherwise we use the relation derived in Appendix B

$$\begin{aligned} & 2\left[\left(\frac{\xi_2}{\xi_1} + \frac{\xi_1}{\xi_2}\right)(k_2 + L + 1) - 2(k_1 + L + 1)\right](k_1, L, \xi_1 | k_2, L, \xi_2) \\ & \quad + \left(\frac{\xi_2}{\xi_1} - \frac{\xi_1}{\xi_2}\right)[(k_2 + 2L + 1)(k_1, L, \xi_1 | k_2 - 1, L, \xi_2) \\ & \quad + (k_2 + 1)(k_1, L, \xi_1 | k_2 + 1, L, \xi_2)] = 0 \end{aligned} \tag{89}$$

to lower k_2 to zero. In such a case we use Eq. (B3) of [16]

$$(k_1 + 1, L, \xi_1 | 0, L, \xi_2) = \frac{k_1 + 2L_1 + 2}{k_1 + 1} \frac{\xi_2 - \xi_1}{\xi_2 + \xi_1} (k_1, L, \xi_1 | 0, L, \xi_2) . \tag{90}$$

6. Open-shell atoms with one valence electron in the Frozen-Core approximation

In the previous Sections we outlined the restricted DHF method for closed-shell atoms. These results can be directly used for the open-shell atoms with one valence electron. The one-particle valence electron hamiltonian is taken in the form of the Fock operator, Eq. (8), where the field of $Z - 1$ core electrons is given by Eq. (10) obtained by solving restricted DHF equations for pertinent closed-shell cation, for instance for Cs^+. This, so called frozen core approximation, is advantageous for later consideration of electron correlation, see e.g. [3].

6.1. PNC amplitude in Cs

The PNC amplitude between 6s and 7s states in Cs is given in the one-particle approximation as [2–6]

$$E_{\mathrm{PNC}} = \langle 7\mathrm{s} | \left[\hat{\mathrm{H}}_{\mathrm{PNC}} \frac{1}{\hat{\mathrm{H}}_{\mathrm{at}} - E_{7\mathrm{s}}} \hat{\mathrm{D}}_z + \hat{\mathrm{D}}_z \frac{1}{\hat{\mathrm{H}}_{\mathrm{at}} - E_{6\mathrm{s}}} \hat{\mathrm{H}}_{\mathrm{PNC}} \right] | 6\mathrm{s} \rangle , \tag{91}$$

where $\hat{\mathrm{H}}_{\mathrm{at}}$ is the one-particle valence electron hamiltonian,

$$\hat{\mathrm{H}}_{\mathrm{at}} - E_{n's} = \mu (Z\alpha)^2 (\hat{\mathrm{f}} - \epsilon_{n's}) , \tag{92}$$

where $\hat{\mathrm{f}}$ is the Fock operator (8), $\hat{\mathrm{D}}_z$ is the third component of the electric dipole operator

$$\hat{\mathrm{D}}_z = \frac{e}{\mu Z \alpha} r n_3 , \tag{93}$$

where e is the elementary electric charge and $\hat{\mathrm{H}}_{\mathrm{PNC}}$ is the parity non-conserving electroweak interaction operator

$$\hat{\mathrm{H}}_{\mathrm{PNC}} = \frac{G_\beta}{\sqrt{8}} Q_W \rho(R) \gamma_5 = \mu (Z\alpha)^3 \frac{\mu^2 G_\beta}{\sqrt{8}} Q_W \rho(r) \gamma_5 , \tag{94}$$

where G_β is the Fermi constant for beta decay,

$$\mu^2 G_\beta \simeq \left(\frac{\mu}{\mu_p}\right)^2 10^{-5} \simeq (0.5446)^2 10^{-11} . \tag{95}$$

Here μ/μ_p is the ratio of electron and proton masses [24]. Further, Q_W is weak charge of the nucleus

$$Q_W = Z(1 - 4\sin^2\theta_W) - N , \tag{96}$$

where Z and N are nucleus charge and number of neutrons, respectively and θ_W is the weak mixing angle; for the case considered

$$Z = 55 , \quad N = 78 . \tag{97}$$

Furthermore, γ_5 is the fifth Dirac matrix in the standard representation and $\rho(R)$ is nucleus charge density (neglecting neutron skin effect) normalized in such a way that

$$\int d^3\boldsymbol{r}\, \rho(r) = 1 . \tag{98}$$

For simplicity we assume the nuclear charge distribution to be that of homogeneous spherical shell

$$\rho(r) = C\Theta(r_N - r) , \quad C = \frac{3}{4\pi r_N^3} , \tag{99}$$

where Θ is the Heaviside function and the constant C was determined from Eq. (98). The charge radius of $^{133}\mathrm{Cs}$ nucleus is [30] $r_N = 4.804\,\mathrm{fm}$. The corresponding value in atomic units is

$$r_N = 4.804 \frac{0.511}{1.973} 10^{-2} Z\alpha \simeq 0.500 \times 10^{-2} . \tag{100}$$

Substituting these equations into Eq. (91) we obtain

$$E_{\mathrm{PNC}} = i \frac{e}{\mu\alpha} \left(-\frac{Q_W}{N}\right) 10^{-11} \mathcal{E}_{\mathrm{PNC}} , \tag{101}$$

where

$$\begin{aligned} \mathcal{E}_{\mathrm{PNC}} = {} & i \frac{(0.5446)^2}{\sqrt{8}} N\alpha \sum_{\mathrm{n}} \langle 7\mathrm{s} | \\ & \times \left\{ \frac{\rho\gamma_5 | \mathrm{np}_{1/2} \rangle \langle \mathrm{np}_{1/2} | r n_3}{\epsilon_{\mathrm{np}_{1/2}} - \epsilon_{7\mathrm{s}}} + \frac{r n_3 | \mathrm{np}_{1/2} \rangle \langle \mathrm{np}_{1/2} | \rho\gamma_5}{\epsilon_{\mathrm{np}_{1/2}} - \epsilon_{6\mathrm{s}}} \right\} | 6\mathrm{s} \rangle . \end{aligned} \tag{102}$$

For the Fock operator, Eq. (8), an important identity

$$[\hat{\mathrm{r}}, \hat{\mathrm{f}}] = \frac{i}{Z\alpha} \gamma_0 \boldsymbol{\gamma} \tag{103}$$

holds. By means of this identity Eq. (102) can be written in the alternative form

$$\mathcal{E}_{\text{PNC}} = \frac{(0.5446)^2}{\sqrt{8}}\frac{N}{Z} \times \sum_{\text{n}} \frac{\langle 7\text{s}|[\rho\gamma_5|\text{np}_{1/2}\rangle\langle\text{np}_{1/2}|\gamma_0\gamma_3 - \gamma_0\gamma_3|\text{np}_{1/2}\rangle\langle\text{np}_{1/2}|\rho\gamma_5]|6\text{s}\rangle}{(\epsilon_{7\text{s}} - \epsilon_{\text{np}_{1/2}})(\epsilon_{6\text{s}} - \epsilon_{\text{np}_{1/2}})}\,. \tag{104}$$

The atomic states in Eqs. (102) and (104) are given by Eqs. (36) and (38)

$$\begin{aligned}\langle \boldsymbol{r}|\, n's\rangle = &\sum_{k=0}^{N} c^{+}_{n's,k} R_{k,|G|-1}(\xi_{n's}, r)\langle \boldsymbol{n}|\, +, +, \frac{1}{2}, \frac{1}{2}\Big\rangle \\ &+ \sum_{k=0}^{N-1} c^{-}_{n's,k} R_{k,|G|}(\xi_{n's}, r)\langle \boldsymbol{n}|\, -, +, \frac{1}{2}, \frac{1}{2}\Big\rangle\end{aligned} \tag{105}$$

and

$$\begin{aligned}\langle \boldsymbol{r}|\, np_{1/2}\rangle = &\sum_{k=0}^{N} c^{+}_{np_{1/2},k} R_{k,|G|-1}(\xi_{p_{1/2}}, r)\langle \boldsymbol{n}|\, -, -, \frac{1}{2}, \frac{1}{2}\Big\rangle \\ &+ \sum_{k=0}^{N-1} c^{-}_{np_{1/2},k} R_{k,|G|}(\xi_{p_{1/2}}, r)\langle \boldsymbol{n}|\, +, -, \frac{1}{2}, \frac{1}{2}\Big\rangle.\end{aligned} \tag{106}$$

6.2. Spinor-angular matrix elements

It follows from Eqs. (26) and (27) that

$$\begin{aligned}&\langle \pm, \kappa, j, m| \begin{pmatrix} 0 & \hat{\text{O}} \\ \hat{\text{O}} & 0 \end{pmatrix} |\pm, -\kappa, j, m\rangle \\ &= i\kappa \frac{\sin\theta}{2}\left[< \hat{\text{O}} >^{\kappa} + < \hat{\text{O}} >^{-\kappa}\right]\end{aligned} \tag{107}$$

and

$$\begin{aligned}&\langle +, \kappa, j, m| \begin{pmatrix} 0 & \hat{\text{O}} \\ \hat{\text{O}} & 0 \end{pmatrix} |-, -\kappa, j, m\rangle \\ &= i\kappa \left[\cos^2\frac{\theta}{2} < \hat{\text{O}} >^{\kappa} + \sin^2\frac{\theta}{2} < \hat{\text{O}} >^{-\kappa}\right],\end{aligned} \tag{108}$$

where

$$< \hat{\text{O}} >^{\kappa} = \langle j, m|^{\kappa}\hat{\text{O}}|j, m\rangle^{\kappa}\,. \tag{109}$$

Here $\hat{\text{O}}$ is either identity matrix or σ_3, the third Pauli spin matrix. The spin operator $\hat{\boldsymbol{S}} = \boldsymbol{\sigma}/2$ is the so(3) vector operator, see e.g. [19], thus

$$\begin{aligned}\langle j, m|^{\kappa}\hat{\text{S}}_3|j, m\rangle^{\kappa} &= \frac{\langle j, m|^{\kappa}\hat{\boldsymbol{S}}\cdot\hat{\boldsymbol{J}}|j, m\rangle^{\kappa}}{j(j+1)}m \\ &= \frac{\kappa\,(2j+1)+1}{4j(j+1)}m\,,\end{aligned} \tag{110}$$

where in the second equality we took advantage of the fact that

$$\begin{aligned}\langle j, m|^{\kappa}\hat{\boldsymbol{S}}\cdot\hat{\boldsymbol{J}}|j, m\rangle^{\kappa} &= \frac{1}{2}\langle j, m|^{\kappa}(\hat{\text{J}}^2 - \hat{\text{L}}^2 + \hat{\text{S}}^2)|j, m\rangle^{\kappa} \\ &= \frac{1}{2}\left[j(j+1) - \left(j - \frac{\kappa}{2}\right)\left(j + 1 - \frac{\kappa}{2}\right) + \frac{3}{4}\right].\end{aligned}$$

It follows from Eqs. (107)-(110) that for the case of interest

$$\left\langle \pm, \kappa, \frac{1}{2}, \frac{1}{2}\middle|\gamma_5\middle|\pm, -\kappa, \frac{1}{2}, \frac{1}{2}\right\rangle = i\kappa\sin\theta = i\kappa Z\alpha\,, \tag{111}$$

$$\left\langle +, \kappa, \frac{1}{2}, \frac{1}{2}\middle|\gamma_5\middle|-, -\kappa, \frac{1}{2}, \frac{1}{2}\right\rangle = i\kappa\,, \tag{112}$$

$$\left\langle \pm, \kappa, \frac{1}{2}, \frac{1}{2}\middle|\gamma_0\gamma_3\middle|\pm, -\kappa, \frac{1}{2}, \frac{1}{2}\right\rangle = i\kappa\frac{\sin\theta}{3} = i\kappa\frac{Z\alpha}{3} \tag{113}$$

and

$$\left\langle +, \kappa, \frac{1}{2}, \frac{1}{2}\middle|\gamma_0\gamma_3\middle|-, -\kappa, \frac{1}{2}, \frac{1}{2}\right\rangle = i\kappa\frac{1 + 2\kappa\cos\theta}{3} \tag{114}$$

In the second equalities in Eqs. (111), (113) we used Eq. (24).

The only non-zero matrix elements of the third component of the unit vector $\boldsymbol{n}$ are

$$\langle g, -\kappa, j, m|n_3|g, \kappa, j, m\rangle = g\cos\theta\langle j, m|^{-\kappa}n_3|j, m\rangle^{\kappa}\,. \tag{115}$$

Since $\boldsymbol{n}$ is the so(3) vector operator

$$\langle j, m|^{-\kappa}n_3|j, m\rangle^{\kappa} = \frac{\langle j, m|^{-\kappa}\boldsymbol{n}\cdot\hat{\boldsymbol{J}}|j, m\rangle^{\kappa}}{j(j+1)}m = -\frac{m}{2j(j+1)}\,, \tag{116}$$

so for the case considered

$$\left\langle g, -\kappa, \frac{1}{2}, \frac{1}{2}\middle|n_3\middle|g, \kappa, \frac{1}{2}, \frac{1}{2}\right\rangle = -\frac{g\cos\theta}{3}\,. \tag{117}$$

6.3. Electroweak matrix elements

The evaluation of the matrix elements $\langle n's|\rho(r)\gamma_5|np_{1/2}\rangle$ is simplified by the fact that the charge distribution $\rho(r)$ is non-vanishing only in the vicinity of the origin, see Eq. (99). Therefore, inside the integral the Sturmian functions can be replaced by their expansion at the origin:

$$\begin{aligned}R_{k,l}(\xi, r) &= \frac{(2\xi)^{l+1}}{\Gamma(2l+2)}\sqrt{\frac{\Gamma(k+2l+2)}{\Gamma(k+1)}}r^l\exp(-\xi r) \\ &\quad\times F(-k, 2l+2, 2\xi r) \\ &= \frac{(2\xi)^{l+1}}{\Gamma(2l+2)}\sqrt{\frac{\Gamma(k+2l+2)}{\Gamma(k+1)}}r^l \\ &\quad\times\sum_{q=0}^{\infty}\frac{(-\xi r)^q}{q!}F(-q, -k, 2l+2, 2)\,.\end{aligned} \tag{118}$$

It then follows from Eqs. (99), (105), (106), (111), (112) and the last equation

$$\begin{aligned}&\langle n's|\rho(r)\gamma_5|np_{1/2}\rangle \\ &\quad= iC\sum_{i,k}\Big[c^{+}_{n',i}c^{+}_{n,k}W^{|G|-1,|G|-1}_{i,k} + Z\alpha c^{+}_{n',i}c^{-}_{n,k}W^{|G|-1,|G|}_{i,k} \\ &\qquad + Z\alpha c^{-}_{n',i}c^{+}_{n,k}W^{|G|,|G|-1}_{i,k} + c^{-}_{n',i}c^{-}_{n,k}W^{|G|,|G|}_{i,k}\Big]\,, \\ &|G| = \sqrt{1 - (Z\alpha)^2}\,,\end{aligned} \tag{119}$$

where

$$\begin{aligned}W^{l_1,l_2}_{i,k} &= \int_0^{r_N} drr^2 R_{i,l_1}(\xi_1 r)R_{k,l_2}(\xi_2 r) \\ &= \sqrt{\frac{\Gamma(i+2l_1+2)}{\Gamma(i+1)}}\sqrt{\frac{\Gamma(k+2l_2+2)}{\Gamma(k+1)}}\frac{(2\xi_1)^{l_1+1}}{\Gamma(2l_1+2)}\frac{(2\xi_2)^{l_2+1}}{\Gamma(2l_2+2)} \\ &\quad\times\sum_{p=0}^{\infty}\frac{r_N^{3+l_1+l_2+p}}{3+l_1+l_2+p}\sum_{q=0}^{p}\frac{(-\xi_1)^q(-\xi_2)^{p-q}}{q!(p-q)!} \\ &\quad\times F(-q, -i, 2l_1+2, 2)F(-p+q, -k, 2l_2+2, 2)\,.\end{aligned} \tag{120}$$

Because of the small value of r_N, Eq. (100), very few terms in the infinite sum over p need to be considered to get a result with working precision.

6.4. Dipole matrix elements

It follows from Eqs. (71), (105), (106), (113), (114) and (117) that

$$\langle n's|\gamma_0\gamma_3|np_{1/2}\rangle = \frac{i}{3}\sum_{i,k} \Big[(1+2\cos\theta)c^{+}_{n',i}c^{+}_{n,k}(i,|G|-1,\xi_{n's}|r|k,|G|-1,\xi_{p_{1/2}}) + Z\alpha c^{+}_{n',i}c^{-}_{n,k}(i,|G|-1,\xi_{n's}|r|k,|G|,\xi_{p_{1/2}}) + Z\alpha c^{-}_{n',i}c^{+}_{n,k}(i,|G|,\xi_{n's}|r|k,|G|-1,\xi_{p_{1/2}}) + (1-2\cos\theta)c^{-}_{n',i}c^{-}_{n,k}(i,|G|,\xi_{n's}|r|k,|G|,\xi_{p_{1/2}})\Big] \tag{120}$$

and

$$\langle n's|rn_3|np_{1/2}\rangle = -\frac{\cos\theta}{3}\sum_{i,k} \Big[c^{+}_{n',i}c^{+}_{n,k}(i,|G|-1,\xi_{n's}|r^2|k,|G|-1,\xi_{p_{1/2}}) - c^{-}_{n',i}c^{-}_{n,k}(i,|G|,\xi_{n's}|r^2|k,|G|,\xi_{p_{1/2}})\Big]\,. \tag{121}$$

The calculation of the radial integrals in the last equation can be by means of Eq. (82) converted to the calculation of integrals (71).

6.5. Hyperfine integrals

The accuracy of the wave function close to the nucleus is usually assessed by calculation of the hyperfine structure splitting. This in turn depends on the radial integral [14]

$$I_{M1} = 2\int_0^\infty dr R^U_n(r) R^L_n(r)\,, \tag{122}$$

where $R^U_n(r)$ and $R^L_n(r)$ are upper and lower radial components of the atomic wave function (36)

$$\langle \mathbf{r}|\,n,\kappa,j,m\rangle = \begin{pmatrix} R^U_n(r)\langle \boldsymbol{n}|j,m\rangle^{\kappa} \\ R^L_n(r)\langle \boldsymbol{n}|j,m\rangle^{-\kappa}\end{pmatrix}, \tag{123}$$

where $\langle \boldsymbol{n}|j,m\rangle^{\kappa}$ are spherical spinors defined in Eq. (21). The pertinent radial integral can be, again, by means of Eq. (82), this time used in the other way, reduced to the known integral (75).

7. Computational details

The described analytic restricted DHF method was implemented in Fortran using LAPACK, the standard linear algebra package.

The most difficult part is the calculation of the radial integrals, Eq. (58). The problem is that there are $2\cdot 2^4\cdot \nu^2$ (ν is the number of shells) sets of integrals to be calculated (the factor 2 is due to Coulomb and exchange interaction, the factor 2^4 is due expansion of the spin-orbitals into two bispinors, see Eq. (36)) and that each set consists of N^4 elements (N stands for the number of basis functions considered for each orbital, cf. Eq. (38)). Specifically, the slowest step is a fourfold loop in the radial functions (i.e. i, k, p, q in Eq. (58)) together with two loops due to the linearization of the product of two functions, see Eq. (59). Computational time required for calculation of the coefficients in Eq. (59) as well as of the radial functions (65) and (66) via the described method is negligible. Unfortunately, the sixfold loop cannot be avoided in principle.

Nevertheless, much time and memory can be spared by considering the symmetries of the problem. First of all, since electrons are, in principle, indistinguishable, it suffices to consider integrals between shells a and b with $b \geq a$. Second, the factor $2^4 = 16$ contains only 10 different sets of integrals (and even less if $a = b$).

Further, a suitable choice of the basis can reduce the computational cost. First, we observed the dependence of the results on the number of functions considered, i.e. for how many functions the results become basis-size-independent. We found that in the case of closed-shell atoms, the number of basis functions for each radial orbital, cf. Eq. (38), is best given by the formula $N_A = 10k_A + q$ where k_A is the number of nodes of the pertinent shell. q is a parameter set to $q = 10\ldots 40$ to obtain basis-size independence, cf. Table B.1. This choice yields results of the same precision as if the inner orbitals were expanded into the same number of functions as the outermost ones.

Second, we could set the screening constants to

$$\xi_A = \frac{1}{n_A}\left(1-\frac{\sigma_A}{Z}\right), \tag{124}$$

where n_A is the non-relativistic principal quantum of the pertinent shell, Z is the nuclear charge and σ_A is number of electrons "sufficiently below" the chosen shell A [32], instead of using $\xi_A = 1/n_A$, Eq. (40). However, while this alternative choice of the screening constants significantly improves the results in the case of neutral atoms for smaller bases and/or heavier atoms, the difference disappears once we require stabilization to ten or more significant digits. Note that the initial oscillations during the SCF cycles are more damped with this alternative choice of ξ.

Finally, running time can be saved by using the OpenMP. In our tests, we found, though, that only the calculation of matrix elements of the two-electron interaction, see Eq. (58), (prior to the SCF procedure), and then the calculation of the mean potential due to the two-electron interaction, see the summation in Eq. (53), in each SCF cycle is worth parallelizing. These two parts are parallelized by pairs of shells (or by shells in the case of the latter), e.g. one CPU calculates all matrix elements between two shells a and b.

We choose hydrogenic orbitals as our initial estimates of orbital coefficients. Alternatively, we could use results for lighter atoms or smaller bases; however, this did not prove to significantly improve the convergence.

Note that the subtraction of the electron rest mass, see Eqs. (8)–(11), is crucial in order to avoid unnecessary loss of precision. As the rest mass is much larger than the binding energies, three to four digits would be lost otherwise due to subtraction of close numbers.

Finally, we would like to mention that the only element in the whole implementation of DHF method calculated in quadruple precision arithmetic is the evaluation of hypergeometric function in Eq. (72), described in Appendix A, as double precision arithmetics did not yield sufficiently accurate results for some values. The needed Γ-function for evaluation of the hypergeometric function, see Appendix A, is evaluated in quadruple precision using the code developed in [33]. The rest of the calculation runs in double precision arithmetic.

8. On the use of the PASC program

This section should give the reader a brief idea about the PASC program and its structure, specifically what kinds of inputs are required and what outputs are to be expected. See the README file for detailed instructions on the compilation and use of the program as well as two example calculations.

The PASC program (Fortran 2008 compliant) can calculate closed-shell DHF atomic systems and open-shell systems with one valence electron in the frozen-core approximation for all systems up to xenon- (54 electrons) and cesium- (55 electrons) like systems. In addition, summation rules, electric dipoles, fine-structure splittings, and PNC amplitude can be calculated. The program can be easily modified, using the present subroutines, to calculate also polarizabilities (scalar, vector, Stark), as well as other related quantities. Also, inclusion of heavier systems is easily achieved by specifying the additional shells.

The desired calculation is specified via an input file (see the README file for a list of all possible parameters). The program prints out the input (system specifications), progress (e.g. convergence of the SCF procedure), as well as final results directly in the terminal. Orbital energies and coefficients (and screening constants, cf. Eqs. (29) and (35)) are saved as textfiles and, once calculated, can be loaded for subsequent calculations of desired quantities such as electric dipoles etc. Note that the program may be easily modified to print out more or less information as well as save also other results, if desired.

9. Results and discussion

Numerical stability of the integrals

The precision of the described methods for calculation of matrix elements is illustrated in Table B.2 for two-particle integrals, Eq. (58), where the most challenging part turned out to be the calculation of one-particle overlap integrals, see Sec. 5.4. The relative error of the two-particle matrix elements lies generally in the interval $10^{-9} - 10^{-14}$. The numerical stability of the proposed method depends on the screening constants and on the orbital quantum numbers as follows. The best results are obtained when the screening constants are all the same, or when they do not significantly differ. The case when they differ and one pair of them equals 1 usually yields the worst results. Similarly, if the orbital quantum numbers l are equal or at least sums of pairs of ls are equal (due to the linearization in Eq. (59)), the method works better than in the cases when they all differ (i.e. for example a matrix element between three positive and one negative energy states).

Restricted DHF for closed-shell atoms

We used the proposed methods of calculation of matrix elements to obtain DHF energies of various systems. First, all closed shell atoms up to xenon were calculated and the obtained results are in an excellent agreement with those published previously [9], see Table B.1 where we list energies for noble gas atoms (for point nuclei). Notice that the results are basis-size-independent and stabilized to ten significant digits. Notice also that our results lie even slightly below the values obtained using numerical integration [9] and that our method is not limited to systems with 20 relativistic shells the most, as is the case of [9], see [34].

Frozen core approximation for Cs

In contrast to the calculation performed in [4,5,14] we considered non-zero size of the nucleus only for the calculation of PNC amplitude, Eqs. (102) and (104). The Sturmian basis set has all the advantages listed in the Introduction, notably it is a complete set on an infinite interval and it has only one artificial parameter, the number N of the considered basis function in Eq. (38). To ascertain the basis (in)dependence of the results, we used N in Eq. (38) up to 150. Also, we studied the dependence of the results on the screening constant $\xi_{n's}$ and $\xi_{p_{1/2}}$ in Eqs. (105) and (106), respectively. We found that the best stabilization of the energies is obtained for $\xi_{p_{1/2}} \simeq 1/19$. For s-states we varied $\xi_{n's}$ from 1/6 to 1/19 and found small dependence of the resulting energies as N in Eq. (38) is sufficiently increased. Good stabilization is achieved for $\xi_{6s} \simeq 1/9$ and $\xi_{7s} \simeq 1/15$.

As it is seen from Table B.3 the agreement between our calculation and those reported in the literature for the ground and excited energies of Cs is very good. The effect of the finite size of the nucleus is found to be negligibly small. In Tables B.4, B.5 and B.6 the calculation of the electric dipole moments, hyperfine integrals and PNC amplitude is compared to those previously reported in literature [4,5,14]. We observed the following dependence of the results on the basis set. To get the stabilization of the ground and low lying excited states energies of Cs to 8 significant digits, it suffices to consider $N = 100$ in Eq. (38). With this basis set one gets stabilization of electric dipole moments to 5 digits (of course the stabilization goes down with increasing the excitation of p-states), of hyperfine integrals to 4 digits and PNC amplitude to 3 digits. We increased the basis set up to $N = 150$ in Eq. (38) to make sure the results are basis independent. We observed that relatively little is gained by increasing the basis set beyond $N = 100$ while performing the calculations in double precision arithmetics. In particular, we found impossible to stabilize the energies to more than 10 significant digits when there are only 16 digits at one's disposal.

The energies and electric dipole moments depend on the behavior of the wave functions on the atomic scale; the effect of the finite size of the nucleus is negligible for both quantities. As it is seen from Table B.4, our results for electric dipole moments significantly differ from those previously reported. This difference cannot be ascribed to the difference in nucleus size. We have shown that the results obtained from our Sturmian based method can be easily converged in the number of the basis functions used yielding stable and basis-independent results. This is not so easy to establish for methods based on non-uniform finite difference [4,5,14]. We conclude that the previous results for electric dipole moments and PNC amplitude are strongly basis dependent.

10. Conclusions

The main contribution of this paper is the development of a numerically stable algorithm for relativistic atomic structure calculations in the Sturmian basis set defined by Eqs. (33) and (35).

Despite the high suitability of the Sturmian basis set for atomic calculations, its use has been hindered by the numerical instability present in the calculation of matrix elements of the Hamilton operator. The herein proposed method allows us to obtain these matrix elements with relative error $10^{-9} - 10^{-15}$, and thus opens the possibility of a wider use of the Sturmian basis set in precise atomic structure calculations. As already mentioned in the introductory section, the use of Sturmian basis set is advantageous for instance, when dealing with highly excited states, autoionizing states and when summation over complete atomic basis set is involved, like in the calculation of atomic polarizabilities and so on. The limitations of the Sturmian basis set encountered in the self-energy problem [35] can be dealt with by the method described in [36]. In brief, the Sturmian basis set is not suitable to describe the highly energetic states belonging to continuum part of the spectra. But these highly energetic states can be in the first approximation treated as free-particles states perturbed by Coulomb potential. One then uses the Sturmian basis set to describe difference between the states of the atomic Hamiltonian and free-particle Hamiltonian perturbed by Coulomb potential.

We illustrated the method on the calculation of the ground and excited energies, the electric dipole moments, hyperfine integrals and PNC amplitude of Cs in the frozen core approximation. Except for the energies, our results significantly differ from those previously reported.

Our next step is to implement the herein proposed algorithm in the coupled-cluster method [37] and its extensions [38] to properly account for electron correlation. We already succeeded in computation of the atomic integrals needed in coupled-cluster method according to the herein proposed scheme. Currently we are working on adaptation of coupled-cluster method and its extension, equation-of-motion-coupled-cluster-method, to spherical symmetry of the atoms. These further developments will be described elsewhere. The extension of herein proposed method from atomic to molecular integrals requires to express in the closed form the coefficients of the expansion of the functions (36) centered at an atom in terms of the functions (36) centered at another atom. This nontrivial issue will be addressed in future.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

Acknowledgements

The support of the grants Q47 Fyzika, Grant SVV 260586 of Charles University, GAUK 339921, and GAČR 20-21179S is gratefully acknowledged. Computational resources were supplied by the project "e-Infrastruktura CZ" (e-INFRA LM2018140) provided within the program Projects of Large Research, Development and Innovations Infrastructures.

Appendix A. Calculation of hypergeometric function

We need to evaluate the hypergeometric function $F(a, b, a+1, -|z|)$, where $a = L_1 + l + 2$, $b = L_1 + L_2 + 3$ and $|z| = \frac{\xi_1}{\xi_2}$, see Eq. (72). For $|z| < 1$ we can evaluate the hypergeometric function through the defining hypergeometric series

$$F(a,b,c,z) = 1 + \frac{ab}{c} z + \frac{a(a+1)b(b+1)}{c(c+1)} \frac{z^2}{2!} + \dots \quad \text{(A.1)}$$

For $|z| > 1$ we use the relation, see e.g. [31],

$$\begin{aligned} &F(a,b,c,z) \\ &= \frac{\Gamma(c)\Gamma(b-a)}{\Gamma(b)\Gamma(c-a)}(1-z)^{-a} F\left(a, c-b, a+1-b, \frac{1}{1-z}\right) \\ &+ \frac{\Gamma(c)\Gamma(a-b)}{\Gamma(a)\Gamma(c-b)}(1-z)^{-b} F\left(b, c-a, b+1-a, \frac{1}{1-z}\right). \end{aligned} \quad \text{(A.2)}$$

For the case considered the hypergeometric function in the first term reduces to $F\left(a, a+1-b, a+1-b, \frac{1}{1-z}\right) = \left(-\frac{z}{1-z}\right)^{-a}$. The hypergeometric function in the second term is then calculated via the series (A.1). For $|z| < \frac{\sqrt{5}-1}{2}$ we evaluate the needed hypergeometric function $F(a, b, a+1, -|z|)$ via the series (A.1), otherwise we use the formula (A.2).

Appendix B. Derivation of difference equation for special one-particle integrals

Substituting $r \to r\xi_1$ in Eq. (33) and multiplying this equation by ξ_1, cf. Eq. (35), we obtain

$$\begin{aligned} &\left[\frac{r}{2\xi_1}\left(\hat{p}_r^2 + \frac{L(L+1)}{r^2}\right) + \frac{\xi_1 r}{2}\right] R_{k_1,L}(\xi_1, r) \\ &= (k_1 + L + 1) R_{k_1,L}(\xi_1, r), \end{aligned} \quad \text{(B.1)}$$

where $k_1 = 0, 1, 2, \dots$ Further, we substitute for the radial functions the expansion

$$R_{k_1,L}(\xi_1, r) = \sum_{k_2=0}^{\infty} c_{k_2} R_{k_2,L}(\xi_2, r). \quad \text{(B.2)}$$

Owing to the orthonormality relations following from the hermiticity of the operator on the lhs of Eq. (B.1) with respect to the inner product with weight r, see [16,19,20] for a more detailed discussion,

$$\int_0^{\infty} dr r R_{k_1,L}(r) R_{k_2,L}(r) = \delta_{k_1,k_2} \quad \text{(B.3)}$$

we get

$$c_{k_2} = \int_0^{\infty} dr r R_{k_1,L}(\xi_1, r) R_{k_2,L}(\xi_2, r). \quad \text{(B.4)}$$

Furthermore, we can write, see Eqs. (27) and (28) of [16],

$$\begin{aligned} \frac{r}{\xi_2}\left(\hat{p}_r^2 + \frac{L(L+1)}{r^2}\right) &= \hat{T}_3^{\xi_2} + \frac{\hat{T}_+^{\xi_2} + \hat{T}_-^{\xi_2}}{2}, \\ \xi_2 r &= \hat{T}_3^{\xi_2} - \frac{\hat{T}_+^{\xi_2} + \hat{T}_-^{\xi_2}}{2}, \end{aligned} \quad \text{(B.5)}$$

where, see Eqs. (26) and (30) of [16],

$$\hat{T}_3^{\xi_2} R_{k,l}(\xi_2 r) = (k + l + 1) R_{k,l}(\xi_2 r) \quad \text{(B.6)}$$

and

$$\begin{aligned} &\hat{T}_\pm^{\xi_2} R_{k,l}(\xi_2 r) = \alpha^\pm(k,l) R_{k\pm1,l}(\xi_2 r), \\ &\alpha^+(k,l) = \sqrt{(k+2l+2)(k+1)}, \\ &\alpha^-(k,l) = \sqrt{k(k+2l+1)}. \end{aligned} \quad \text{(B.7)}$$

By substituting Eq. (B.2) into Eq. (B.1) and using Eq. (B.5), we rewrite Eq. (B.1) into the form

$$\begin{aligned} &\sum_{k_2}\left[\frac{\xi_2}{2\xi_1}\left(\hat{T}_3^{\xi_2} + \frac{\hat{T}_+^{\xi_2} + \hat{T}_-^{\xi_2}}{2}\right)\right. \\ &\left. + \frac{\xi_1}{2\xi_2}\left(\hat{T}_3^{\xi_2} - \frac{\hat{T}_+^{\xi_2} + \hat{T}_-^{\xi_2}}{2}\right) - (k_1 + L + 1)\right] c_{k_2} R_{k_2,L}(\xi_2, r) = 0. \end{aligned} \quad \text{(B.8)}$$

Using Eqs. (B.6) and (B.7) we further rewrite the last equation as

$$\begin{aligned} &\sum_{k_2}\left\{\left[\left(\frac{\xi_2}{\xi_1} + \frac{\xi_1}{\xi_2}\right)(k_2 + L + 1) - (k_1 + L + 1)\right] R_{k_2,L}(\xi_2, r)\right. \\ &+ \left[\frac{\alpha^+(k_2, L)}{2} R_{k_2+1,L}(\xi_2, r) + \frac{\alpha^-(k_2, L)}{2} R_{k_2-1,L}(\xi_2, r)\right] \\ &\left.\times\left(\frac{\xi_2}{\xi_1} - \frac{\xi_1}{\xi_2}\right)\right\} c_{k_2} = 0. \end{aligned} \quad \text{(B.9)}$$

Finally, using now the orthonormality relations (B.3) we get from the last equation a difference equation for the coefficients c_{k_2}

Table B.1

Total DHF energies (in atomic units) of noble gas atoms (with point nuclei). For each shell we consider $10n+q$ basis functions; n denotes the number of nodes of the shell and q is an integer parameter. The bottom line shows values obtained from the program GRASP2K [9]. Notice that our results lie slightly below those values.

q	He	Ne	Ar	Kr	Xe
10	−2.8618135601	−128.6903260183	−528.6795435479	−2788.88069683	−7447.14851799
15	−2.8618133441	−128.6919589740	−528.6842614909	−2788.88452684	−7447.16037332
20	−2.8618133422	−128.6919693976	−528.6844431116	−2788.88481388	−7447.16237271
25	−2.8618133422	−128.6919694959	−528.6844502460	−2788.88483361	−7447.16267835
30	−2.8618133422	−128.6919694947	−528.6844504477	−2788.88483467	−7447.16272247
35	−2.8618133422	−128.6919694947	−528.6844504564	−2788.88483474	−7447.16272863
40	−2.8618133422	−128.6919694947	−528.6844504565	−2788.88483472	−7447.16272924
GRASP	−2.8618133402	−128.6919693843	−528.6844498188	−2788.884831	−7447.16271867

Table B.2

Illustration of the accuracy of the method for calculation of the radial integrals, Eq. (58). $\mathcal{R}(\{i,p,k,q\},l)$ stands for $\mathcal{R}(\{i,l_1,\xi_1\},\{p,l_2,\xi_2\},\{k,l_3,\xi_3\},\{q,l_4,\xi_4\},l)$. The listed integrals l_i are used in the calculation of xenon atom, see Table B.1 Note that the orbital quantum numbers l are not displayed here to all significant digits. The relative errors are errors of the computation in double precision relative to that in quadruple precision.

	$\mathcal{R}(\{i,p,k,q\},l)$	rel. err.
1	$2.96878481326560 \cdot 10^{1}$	$0.13 \cdot 10^{-14}$
2	$-2.96828547437140 \cdot 10^{1}$	$0.46 \cdot 10^{-9}$
3	$9.24214621921513 \cdot 10^{1}$	$0.15 \cdot 10^{-14}$
4	$9.28341528143204 \cdot 10^{1}$	$0.25 \cdot 10^{-14}$
5	$7.01043778797756 \cdot 10^{1}$	$0.28 \cdot 10^{-11}$
6	$2.63170349316775 \cdot 10^{0}$	$0.34 \cdot 10^{-13}$
7	$-1.12288474479141 \cdot 10^{-2}$	$0.19 \cdot 10^{-11}$
8	$3.34796422857836 \cdot 10^{0}$	$0.26 \cdot 10^{-13}$
9	$-3.02772710163331 \cdot 10^{-3}$	$0.49 \cdot 10^{-10}$

	i	l_1	ξ_1	p	l_2	ξ_2	k	l_3	ξ_3	q	l_4	ξ_4	l
1	49	−0.08091	1	49	−0.08091	1	49	−0.08091	1	49	−0.08091	1	0
2	49	0.91909	1	49	−0.08091	1	49	−0.08091	1	49	−0.08091	1	0
3	49	1.97401	1/3	49	2.97401	1/3	49	1.97401	1/3	49	2.97401	1/3	0
4	49	1.97401	1/3	49	2.97401	1/3	49	2.97401	1/3	49	1.97401	1/3	0
5	49	1.96080	1/2	49	2.97401	1/3	49	0.96080	1/2	49	1.97401	1/3	0
6	49	1.96080	1/2	49	2.97401	1/3	49	1.97401	1/3	49	0.96080	1/2	1
7	49	1.96080	1/2	29	2.97401	1/3	39	0.96080	1/2	44	1.97401	1/3	0
8	49	1.96080	1/2	29	2.97401	1/3	44	1.97401	1/3	39	0.96080	1/2	1
9	49	−0.08091	1	29	2.97401	1/3	39	0.91909	1	44	1.97401	1/3	2

Table B.3

Excited one-particle energies of Cs in atomic units. For comparison with other results we use the same nomenclature as in [14]; FD stands for finite difference code; DKB for dual kinetic basis set code [15] and ND for Notre Dame code [11]. The reference [5] uses the basis set described in [14].

	$6s$	$7s$	$6p_{1/2}$	$7p_{1/2}$	$8p_{1/2}$
this work	−0.1273734422(1)	−0.0551888581(1)	−0.085615749	−0.0420213429	−0.0251204371(1)
FD	−0.127368	−0.05518735	−0.08561589		
DKB	−0.1273674	−0.05518714	−0.08561576		
ND	−0.1273682	−0.0551875	−0.08561616		
[5]	−0.127368	−0.0551863	−0.0856135	−0.042023	

Table B.4

Reduced dipole matrix elements $(n's|D|np_{1/2})$ in atomic units; $(n's|D|np_{1/2}) = (n's|z|np_{1/2})\sqrt{2}/(1/2,1/2,1,0|1/2)$.

		$6p_{1/2}$	$7p_{1/2}$	$8p_{1/2}$
this work	$6s$	5.0367970	0.30564910	0.0956989
[5]		5.2777	0.3717	
this work	$7s$	4.2458375	10.789637	0.857288
[5]		4.4131	11.009	

Table B.5

Hyperfine integrals (122) in atomic units.

	$6s$ ($\times 10^{-1}$)	$7s$ ($\times 10^{-2}$)	$6p_{1/2}$ ($\times 10^{-2}$)
this work	1.14301	3.1410	−1.25543
FD	1.114751	3.063077	−1.252026
DKB	1.114741	3.063069	−1.252018
ND	1.121812	3.084164	−1.218362

Table B.6

PNC amplitude (102), (104) in frozen core DHF approximation.

	$\mathcal{A}_{\text{PNC}}$
this work	0.8097
FD	0.74
DKB	0.7395
ND	0.8546

$$\left[\left(\frac{\xi_2}{\xi_1}+\frac{\xi_1}{\xi_2}\right)(k_2+L+1)-(k_1+L+1)\right]c_{k_2} + \left(\frac{\xi_2}{\xi_1}-\frac{\xi_1}{\xi_2}\right)\left[\alpha^{+}(k_2-1,L)c_{k_2-1}+\alpha^{-}(k_2+1,L)c_{k_2+1}\right]=0. \tag{B.10}$$

Eliminating now the normalization factors

$$c_{k_2} = \sqrt{\frac{k_2!}{(k_2+2L+1)!}}\,\tilde{c}_{k_2}\,, \tag{B.11}$$

we have from Eqs. (68) and (B.4)

$$\tilde{c}_{k_2} = (k_1, L, \xi_1 | k_2, L, \xi_2)\,. \tag{B.12}$$

The last three equations then yield Eq. (89).

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