

Relativistic central-field Green's functions for the RATIP package

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Abstract

From perturbation theory, Green's functions are known for providing a simple and convenient access to the (complete) spectrum of atoms and ions. Having these functions available, they may help carry out perturbation expansions to any order beyond the first one. For most realistic potentials, however, the Green's functions need to be calculated numerically since an analytic form is known only for *free* electrons or for their motion in a pure Coulomb field. Therefore, in order to facilitate the use of Green's functions also for atoms and ions other than the hydrogen-like ions, here we provide an extension to the RATIP program which supports the computation of relativistic (one-electron) Green's functions in an — arbitrarily given — central-field potential $V(r)$. Different computational modes have been implemented to define these effective potentials and to generate the radial Green's functions for all bound-state energies $E < 0$. In addition, care has been taken to provide a user-friendly component of the RATIP package by utilizing features of the Fortran 90/95 standard such as data structures, allocatable arrays, or a module-oriented design.

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PROGRAM SUMMARY

Title of program: XGREENS.

Catalogue number: To be assigned.

Program obtainable from: CPC Program Library, Queen's University of Belfast, N. Ireland. Users may also down-load a tar-file of the program `ratip00.tar` from our home page at the University of Kassel (<http://www.physik.uni-kassel.de/fritzsche/programs.html>).

Licensing provisions: None.

Computer for which the new version has been tested: PC Pentium II, III, IV, Athlon.

Installations: University of Kassel (Germany).

Operating systems: SuSE Linux 8.2, SuSE Linux 9.0.

Program language used in the new version: ANSI standard Fortran 90/95.

Memory required to execute with typical data: On a standard grid (400 nodes), one central-field Green's function requires about 50 kBytes in RAM while approximately 3 MBytes are needed if saved as two-dimensional array on some external disc space.

No. of bits in a word: Real variables of double- and quad-precision are used.

Peripheral used: Disk for input/output.

CPU time required to execute test data: 2 minutes on a 450 MHz Pentium III processor.

Distribution format: compressed tar file.

Keywords: Central-field Green's function, confluent hypergeometric function, Coulomb Green's function, Kummer function, multi-configuration Dirac-Fock, regular and irregular solutions.

Nature of the physical problem: In atomic perturbation theory, Green's functions may help carry out the summation over the complete spectrum of atom and ions, including the (summation over the) bound states as well as an integration over the continuum [1]. Analytically, however, these functions are known only for *free* electrons ($V(r) \equiv 0$) and for electrons in a *pure* Coulomb field ($V(r) = -Z/r$). For all other choices of the potential, in contrast, the Green's functions must be determined numerically.

Method of solution: Relativistic Green's functions are generated for an arbitrary central-field potential $V(r) = -Z(r)/r$ by using a piecewise linear approximation of the effective nuclear charge function $Z(r)$ on some grid r_i ($i = 1, \dots, N$): $Z_i(r) = Z_{0i} + Z_{1i} r$. Then, following McGuire's algorithm [2], the radial Green's functions are constructed from the (two) linear-independent solutions of the homogeneous equation [3]. In the computation of these radial functions, the Kummer and Tricomi functions [4] are used extensively.

Restrictions onto the complexity of the problem: The main restrictions of the program concern the shape of the effective nuclear charge $Z(r) = -r V(r)$, i. e. the choice of the potential,

and the allowed energies. Apart from obeying the proper boundary conditions for a point-like nucleus, namely, $Z(r \rightarrow 0) = Z_{\text{nuc}} > 0$ and $Z(r \rightarrow \infty) = Z_{\text{nuc}} - N_{\text{electrons}} \geq 0$, the first derivative of the charge function $Z(r)$ must be smaller than the (absolute value of the) energy of the Green's function, $\frac{\partial Z(r)}{\partial r} < |E|$.

Unusual features of the program: XGREENS has been designed as a part of the RATIP package [5] for the calculation of relativistic atomic transition and ionization properties. In a short dialog at the beginning of the execution, the user can specify the choice of the potential as well as the energies and the symmetries of the radial Green's functions to be calculated. Apart from central-field Green's functions, of course, the Coulomb Green's function [6] can also be computed by selecting a constant nuclear charge $Z(r) = Z_{\text{eff}}$. In order to test the generated Green's functions, moreover, we compare the two lowest bound-state orbitals which are calculated from the Green's functions with those as generated separately for the given potential. Like the other components of the RATIP package, XGREENS makes careful use of the Fortran 90/95 standard.

References:

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LONG WRITE-UP

1 Introduction

The use of Green's function has a long tradition for solving physical problems, both in classical and quantum physics. From perturbation theory, for instance, these functions are known for providing a rather simple access to the complete spectrum of a quantum system and, hence, to facilitate the computation of perturbation expansions beyond the first order in perturbation theory. Applications of the Green's functions can be therefore found not only in atomic and molecular physics but also in quantum optics, field theory, solid-state physics, and at various place elsewhere.

In atomic physics, however, the use of Green's function methods was so far mainly restricted to describe the motion of electrons in a pure Coulomb field, i. e. to the theory of hydrogen and hydrogen-like ions. For these one-electron systems, calculations have been carried out, for example, for the two-photon [1, 2] and multi-photon ionization [3, 4], the two-photon decay [5], the second-order contributions to the atomic polarizabilities [6] as well as for determining radiative corrections [7, 8].

Less attention, in contrast, has been paid to utilize Green's functions for non-Coulomb fields or for describing the properties of many-electron atoms and ions. Unlike to the generation of the — bound and free-electron — wave functions to the Schrödinger and Dirac equation, for which a number of programs are available now also within the CPC-library [9, 10], there is almost no code freely available which helps generate the relativistic central-field Green's functions. As known from the literature, however, nonrelativistic central-field Green's functions were constructed by McGuire [11] and by Huillier and coworkers [12], and were successfully applied for studying the multi-photon ionization of valence-shell electrons in alkali atoms. Therefore, in order to facilitate the use of relativistic central-field Green's functions for atomic computations, here we describe and provide an extension to the RATIP package which calculates these functions (as the solution of the Dirac equation with a δ -like inhomogeneity) for an arbitrary central field $V(r)$.

In the following section, we start with summarizing the basic formulas for the computation of relativistic central-field Green's functions. Apart from a brief discussion of the Dirac Hamiltonian, this includes the *defining equation* for central-field Green's function and the separation of the three-dimensional Green's function into radial and angular parts. However, since the separation has been discussed in detail elsewhere in the literature [13], we restrict ourselves to a short account on that topic and mainly focus on the computation of the radial components of the Green's functions. Section 3 later describes the program structure of XGREENS, its interactive control and how the code is distributed. Because the XGREENS program is designed as part of the RATIP package, we have used and modified several modules which were published before along with other components of the program. Section 4 explains and displays two examples of XGREENS, including (a) a dialog in order to calculate a central-field potential from GRASP92 wave functions [9] and (b) the generation of the radial Green's functions if the potential is loaded from an external file. Finally, a short summary and outlook is given in section 5.

2 Theoretical background

2.1 Relativistic central-field Green's functions

Most naturally, the relativistic central-field Green's function can be considered as a generalization of the (relativistic) Coulomb Green's function if, in the Dirac Hamiltonian¹

$$\hat{H}_D(\mathbf{r}) = -i\alpha\nabla + \beta c^2 + V(r), \quad (1)$$

the Coulomb potential is replaced by some (arbitrarily given) central-field potential, $V^C(r) = -\frac{Z}{r} \rightarrow -\frac{Z(r)}{r}$. As in the nonrelativistic case where the Green's function obeys the *defining* equation $(\hat{H} - E)G_E(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}')$, the relativistic Green's function is given by a 4×4 matrix [14] which satisfies the inhomogeneous equation

$$\left(\hat{H}_D(\mathbf{r}) - E - c^2\right) G_E(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}') \mathbf{I}_4, \quad (2)$$

with \mathbf{I}_4 being the 4×4 unit-matrix and where, as usual in atomic structure theory, E refers to the total energy of the electron but without its rest energy $m_e c^2$. Moreover, since in polar coordinates a central-field potential $Z(r)$ in the Hamiltonian (1) does not affect the separation of the variables, the central-field Green's function has the same *radial-angular* representation as in the pure Coulomb case [13]

$$G_E(\mathbf{r}, \mathbf{r}') = \sum_{\kappa m} \frac{1}{rr'} \begin{pmatrix} g_{E\kappa}^{LL}(r, r') \Omega_{\kappa m}(\hat{\mathbf{r}}) \Omega_{\kappa m}^\dagger(\hat{\mathbf{r}}') & -i g_{E\kappa}^{LS}(r, r') \Omega_{\kappa m}(\hat{\mathbf{r}}) \Omega_{-\kappa m}^\dagger(\hat{\mathbf{r}}') \\ i g_{E\kappa}^{SL}(r, r') \Omega_{-\kappa m}(\hat{\mathbf{r}}) \Omega_{\kappa m}^\dagger(\hat{\mathbf{r}}') & g_{E\kappa}^{SS}(r, r') \Omega_{-\kappa m}(\hat{\mathbf{r}}) \Omega_{-\kappa m}^\dagger(\hat{\mathbf{r}}') \end{pmatrix}, \quad (3)$$

where $\Omega_{\kappa m}(\hat{\mathbf{r}}) = \Omega_{\kappa m}(\vartheta, \varphi)$ denotes a standard spherical Dirac-spinor and $\kappa = \pm(j + 1/2)$ for $l = j \pm 1/2$ is the *relativistic* angular momentum quantum number; this number carries information about both the total angular momentum j as well as the parity $(-1)^l$ of the Green's function. While the summation over $\kappa = \pm 1, \pm 2, \dots$ runs over all (non-zero) integers, the summation over the magnetic quantum number $m = -j, -j + 1, \dots, j$ is restricted by the corresponding total angular momentum. Moreover, the radial part of the central-field Green's function $\begin{pmatrix} g_{E\kappa}^{LL}(r, r') & g_{E\kappa}^{LS}(r, r') \\ g_{E\kappa}^{SL}(r, r') & g_{E\kappa}^{SS}(r, r') \end{pmatrix}$ in (3) can be treated simply as a 2×2 matrix function which satisfies the equation

$$\begin{pmatrix} \left[-\frac{\alpha Z(r)}{r} - \alpha E \right] & \left[\frac{\kappa}{r} - \frac{\partial}{\partial r} \right] \\ \left[\frac{\partial}{\partial r} + \frac{\kappa}{r} \right] & \left[-\frac{2}{\alpha} - \frac{\alpha Z(r)}{r} - \alpha E \right] \end{pmatrix} \begin{pmatrix} g_{E\kappa}^{LL} & g_{E\kappa}^{LS} \\ g_{E\kappa}^{SL} & g_{E\kappa}^{SS} \end{pmatrix} = \alpha \delta(r - r') \mathbf{I}_2, \quad (4)$$

with \mathbf{I}_2 now being the 2×2 unit-matrix. Note that in Eq. (4), α refers to Sommerfeld's fine structure constant and that, in order to keep the equations similar to those for the Coulomb Green's functions [13], we make use of a nuclear charge function $Z(r) = -rV(r)$ to define the central-field potential, instead of $V(r)$ explicitly. In the radial-angular representation (3), two superscripts T and T' were introduced to denote the individual components in the 2×2 radial Green's function matrix. These superscripts take the values $T = L$ or $T = S$ to refer to

¹Here and in the following, we use atomic units ($m_e = \hbar = e^2/4\pi\epsilon_0 = 1$) if not stated otherwise.

either the *large* or *small* component, respectively, when multiplied with a corresponding (2–spinor) radial solution of the Dirac Hamiltonian (1). For a pure Coulomb potential, $Z(r) \equiv Z_{\text{eff}}$, an explicit representation of the (four) components $g_{E\kappa}^{TT'}(r, r')$ of the radial Green's function can be found in Refs. [13, 14, 15].

2.2 Generation of radial Green's functions

When compared with the Coulomb Green's functions, not much need to be changed for the central–field functions in Eqs. (3) and (4) except that the nuclear charge $Z = Z(r)$ now depends on r and, hence, that *analytic solutions* to these equations are no longer available. Therefore, to find a numerical solution to Eq. (4), let us first mention that this matrix equation just describes *coupled* equations for the two independent pairs $(g_{E\kappa}^{LL}, g_{E\kappa}^{SL})$ and $(g_{E\kappa}^{SS}, g_{E\kappa}^{LS})$ of the radial components. For example, if we consider the first pair $(g_{E\kappa}^{LL}, g_{E\kappa}^{SL})$ of radial components of the Green's function, it has to satisfy the two equations

$$\left[-\frac{\alpha Z(r)}{r} - \alpha E \right] g_{E\kappa}^{LL}(r, r') + \left[\frac{\kappa}{r} - \frac{\partial}{\partial r} \right] g_{E\kappa}^{SL}(r, r') = \alpha \delta(r - r'), \quad (5)$$

$$\left[\frac{\partial}{\partial r} + \frac{\kappa}{r} \right] g_{E\kappa}^{LL}(r, r') + \left[-\frac{2}{\alpha} - \frac{\alpha Z(r)}{r} - \alpha E \right] g_{E\kappa}^{SL}(r, r') = 0, \quad (6)$$

and a similar set of equations holds for the second pair $(g_{E\kappa}^{SS}, g_{E\kappa}^{LS})$. In the following, therefore, we will discuss the algorithm for solving Eqs. (5) and (6) but need not display the analogue formulas for the pair $(g_{E\kappa}^{SS}, g_{E\kappa}^{LS})$.

Inserting $g_{E\kappa}^{SL}(r, r')$ from Eq. (6) into (5), we arrive at the second–order inhomogeneous differential equation

$$\left(\frac{\partial}{\partial r} - \frac{\kappa}{r} \right) \frac{\left(\frac{\partial}{\partial r} + \frac{\kappa}{r} \right) g_{E\kappa}^{LL}(r, r')}{\frac{2}{\alpha} + \frac{\alpha Z(r)}{r} + \alpha E} + \left(\frac{\alpha Z(r)}{r} + \alpha E \right) g_{E\kappa}^{LL}(r, r') = \alpha \delta(r - r') \quad (7)$$

for the component $g_{E\kappa}^{LL}(r, r')$. Solution of this equation can be constructed as product of two linearly independent solutions [14]

$$g_{E\kappa}^{LL}(r, r') = M_{E\kappa}^{LL}(\min(r, r')) \cdot W_{E\kappa}^{LL}(\max(r, r')) \quad (8)$$

for the corresponding homogeneous case [cf. Eq. (10) below], where $M_{E\kappa}^{LL}(r)$ denotes a solution which is regular at the origin, and $W_{E\kappa}^{LL}(r)$ a solution regular at infinity. Below, we will obtain these functions following the numerical procedure as suggested by McGuire [11].

For this, let us start with approximating the nuclear charge function $Z(r)$ on some grid r_i , $i = 1, \dots, i_{\text{max}}$ in terms of a set of straight lines

$$Z_i(r) = Z_{0i} + Z_{1i} r, \quad \text{for } r_i \leq r \leq r_{i+1}, \quad (9)$$

and from the *homogeneous part* of Eq. (7)

$$\left(\frac{\partial}{\partial r} - \frac{\kappa}{r} \right) \frac{\left(\frac{\partial}{\partial r} + \frac{\kappa}{r} \right) g_{E\kappa}^i(r)}{\frac{2}{\alpha} + \frac{\alpha Z_i(r)}{r} + \alpha E} + \left(\frac{\alpha Z_i(r)}{r} + \alpha E \right) g_{E\kappa}^i(r) = 0 \quad (10)$$

as given for the i -th interval $[r_i, r_{i+1}]$ of the grid. In this Eq., we can drop the second argument r' in the component $g_{E\kappa}^{LL}$, since it now appears only as a parameter, and replace it by the superscript i to denote the particular piece of the grid for which we want the solution. From the approximation (9), moreover, we see that the nuclear charge function $Z_i(r)$ within the i -th interval gives rise to a *pure* Coulomb potential Z_{0i}/r and a constant which is simply *added* to the energy: $E \rightarrow Z_{0i} + E$. We therefore find that, within the given interval, the regular and irregular solutions at the origin in (8) can both be written as linear combinations of the corresponding solutions for a Coulomb field

$$M_{E\kappa}^i(r) = f_{i,1} M_{E\kappa}^{i,\text{Coulomb}}(r) + f_{i,2} W_{E\kappa}^{i,\text{Coulomb}}(r) \quad (11)$$

$$W_{E\kappa}^i(r) = g_{i,1} M_{E\kappa}^{i,\text{Coulomb}}(r) + g_{i,2} W_{E\kappa}^{i,\text{Coulomb}}(r) \quad (12)$$

with constants $\{f_{i,1}, f_{i,2}, g_{i,1}, g_{i,2}\}$ which still need to be determined. For the Coulomb potential, the functions $M_{E\kappa}^{i,\text{Coulomb}}(r)$ and $W_{E\kappa}^{i,\text{Coulomb}}(r)$ are known analytically and given by [14]

$$M_{E\kappa}^{i,\text{Coulomb}}(r) = r^{s_i} e^{-q_i r} [t_i M(-t_i + 1, 2s_i + 1, 2q_i r) + (\kappa - Z_{0i}/q_i) M(-t_i, 2s_i + 1, 2q_i r)], \quad (13)$$

$$W_{E\kappa}^{i,\text{Coulomb}}(r) = r^{s_i} e^{-q_i r} [(\kappa + Z_{0i}/q_i) U(-t_i + 1, 2s_i + 1, 2q_i r) + U(-t_i, 2s_i + 1, 2q_i r)], \quad (14)$$

where $M(a, b, r)$ and $U(a, b, r)$ denote the Kummer and Tricomi functions [16, 17], respectively, and where the quantities s_i , t_i and q_i are given by

$$s_i = \sqrt{\kappa^2 - \alpha^2 Z_{0i}^2}, \quad t_i = \frac{\alpha Z_{0i}((E + Z_{1i})\alpha^2 + 1)}{\sqrt{1 - ((E + Z_{1i})\alpha^2 + 1)^2}} - s_i, \quad (15)$$

$$q_i = \sqrt{-(E + Z_{1i})((E + Z_{1i})\alpha^2 + 2)}. \quad (16)$$

The set of constants $\{f_{i,1}, f_{i,2}, g_{i,1}, g_{i,2}; i = 1, \dots, i_{\max}\}$ can be determined from the fact that the two functions $M_{E\kappa}^{LL}(r)$ and $W_{E\kappa}^{LL}(r)$ in ansatz (8) as well as their derivatives need to be continuous in r , and that they behave *regularly* at the origin or at infinity, respectively. The constraint of being regular at the origin, for instance, requires the coefficients $f_{i=1,1} = 1$ and $f_{i=1,2} = 0$ and can be used together with the continuity $M_{E\kappa}^{LL}(r)$ and $M_{E\kappa}'^{LL}(r)$,

$$f_{i,1} M_{E\kappa}^{i,\text{C}}(r_i) + f_{i,2} W_{E\kappa}^{i,\text{C}}(r_i) = f_{i+1,1} M_{E\kappa}^{i+1,\text{C}}(r_i) + f_{i+1,2} W_{E\kappa}^{i+1,\text{C}}(r_i), \quad (17)$$

$$f_{i,1} M_{E\kappa}'^{i,\text{C}}(r_i) + f_{i,2} W_{E\kappa}'^{i,\text{C}}(r_i) = f_{i+1,1} M_{E\kappa}'^{i+1,\text{C}}(r_i) + f_{i+1,2} W_{E\kappa}'^{i+1,\text{C}}(r_i). \quad (18)$$

[where the superscript C here refers to the Coulomb functions in Eqs. (13) and (14)] in order to determine all the coefficients $f_{i,j}$ up to a normalization constant. A similar recurrence procedure also applies to the coefficients $g_{i,j}$, but by starting from 'infinity', that is with $g_{i_{\max},1} = 0$ and $g_{i_{\max},2} = 1$, and by going *backwards* in the index i towards the origin.

To determine finally the normalization of the radial component $g_{E\kappa}^{LL}(r, r')$, e. g. of the coefficients $\{f_{i,j}, g_{i,j}\}$, we may return to Eq. (7) and re-write it in the form

$$\left(\hat{h}_0 - E\right) g_{E\kappa}^{LL}(r, r') = \delta(r - r'). \quad (19)$$

Taking the integral over latter equation, we see that

$$\int_{r'-\varepsilon}^{r'+\varepsilon} (\hat{h}_0 - E) g_{E\kappa}^{LL}(r, r') dr = \int_{r'-\varepsilon}^{r'+\varepsilon} \delta(r - r') dr = 1$$

should be valid for $\varepsilon \rightarrow +0$ and for any r' and, hence, that — by using Eq. (7) and carrying out some algebraic manipulations — the derivative

$$\left. \frac{\partial}{\partial r} g_{E\kappa}^{LL}(r, r') \right|_{r=r'-\varepsilon}^{r=r'+\varepsilon} = \alpha \left(\frac{2}{\alpha} + \frac{\alpha Z(r')}{r'} + \alpha E \right) \quad (20)$$

'jumps' at $r = r'$. We can use the right hand side of Eq. (20) together with the derivative of Eq. (8) to determine the normalization constants c_f and c_g with which the coefficients $f_{i,j}$ and $g_{i,j}$ need to be multiplied in order to obtain the normalized radial component $g_{E\kappa}^{LL}(r, r')$.

Having constructed $g_{E\kappa}^{LL}(r, r')$ piecewise as solution to Eq. (7), we may obtain the second component $g_{E\kappa}^{SL}(r, r')$ of this pair simply from Eq. (6),

$$g_{E\kappa}^{SL}(r, r') = \frac{\left(\frac{\partial}{\partial r} + \frac{\kappa}{r} \right) g_{E\kappa}^{LL}(r, r')}{\frac{2}{\alpha} + \frac{\alpha Z(r)}{r} + \alpha E}, \quad (21)$$

where the derivatives of the Kummer and Tricomi functions in expressions (13) and (14) can be calculated by means of standard formulae [17]

$$M'(a, b, z) = \frac{a}{b} M(a + 1, b + 1, z), \quad U'(a, b, z) = -a U(a + 1, b + 1, z).$$

In practise, both functions $M(a, b, z)$ and $U(a, b, z)$ are required only for real arguments a , b , and z but need to be calculated with a rather sophisticated algorithm [18] in order to ensure numerical stability and to provide sufficiently accurate results. A similar numerical procedure has to be carry out also for the second pair $(g_{E\kappa}^{SS}, g_{E\kappa}^{LS})$ of radial components. This gives rise of course to another set of coefficients $\{\tilde{f}_{i,j}, \tilde{g}_{i,j}\}$ and, finally, to the full radial Green's function from Eq. (4). The $4i_{\max}$ coefficients for the (piecewise) regular and irregular solutions in ansatz (11–12) and (8) certainly provide — together with a few numerical procedures — the most *compact* representation of the radial central–field Green's functions. For the further computation of matrix elements and atomic properties, however, these radial components are usually represented (and stored) at some (2–dimensional) grid in r and r' as we will discuss below.

2.3 Tests on the accuracy of the radial Green's functions

To make further use of the Green's functions in applications, it is necessary to have a simple test on their *numerical* accuracy. For the radial–spherical representation of these functions as defined in Eq. (3), such a test is easily constructed since the Green's function contains the information about the complete spectrum of the Hamiltonian (1) and, hence, about any of its eigenstates $\psi_n(\mathbf{r})$. Making use of the well–known expansion of the Green's function

$$G_E(\mathbf{r}, \mathbf{r}') = \sum_n \frac{\psi_n(\mathbf{r}) \psi_n^\dagger(\mathbf{r}')}{E_n - E}$$

in terms of the eigenstates of the Hamiltonian, the relation

$$\psi_n(\mathbf{r}') = (E_n - E) \int d\mathbf{r} \psi_n^\dagger(\mathbf{r}) G_E(\mathbf{r}, \mathbf{r}') \quad (22)$$

can be easily derived from the orthogonality of the eigenfunctions and holds for all energies $E \neq E_n$. With the representation (3) in mind, the relation (22) can be written also in terms of the radial wave and Green's functions

$$\begin{pmatrix} \tilde{P}_{n\kappa}(r') \\ \tilde{Q}_{n\kappa}(r') \end{pmatrix} = (E_{n\kappa} - E) \int_0^\infty dr (P_{n\kappa}(r), Q_{n\kappa}(r)) \begin{pmatrix} g_{E\kappa}^{LL}(r, r') & g_{E\kappa}^{LS}(r, r') \\ g_{E\kappa}^{SL}(r, r') & g_{E\kappa}^{SS}(r, r') \end{pmatrix}, \quad (23)$$

where $P_{n\kappa}(r)$ and $Q_{n\kappa}(r)$ are the large and small components of the (Dirac) radial 2-spinors. As indicated by the tilde on the left-hand-side of Eq. (23), therefore, this relation may serve as a test on the accuracy of the Green's functions if, for instance, the radial components from both side of the equation are compared with each other or if some proper *overlap* integral is calculated.

To test on the precision of the Green's functions in XGREENS, we generate the radial bound-state wave function $P_{n\kappa}(r)$ and $Q_{n\kappa}(r)$ as solution of the radial Dirac equation

$$\left[-\frac{\alpha Z(r)}{r} - \alpha E \right] P_{n\kappa}(r) + \left[\frac{\kappa}{r} - \frac{\partial}{\partial r} \right] Q_{n\kappa}(r) = 0 \quad (24)$$

$$\left[\frac{\partial}{\partial r} + \frac{\kappa}{r} \right] P_{n\kappa}(r) + \left[-\frac{2}{\alpha} - \frac{\alpha Z(r)}{r} - \alpha E \right] Q_{n\kappa}(r) = 0 \quad (25)$$

with the same potential $-\frac{Z(r)}{r}$ as applied before and by making use of the program by Salvat *etal* [10]. This solver has been embedded in our code and is utilized in order to calculate the relativistic components. With these radial functions, we then compute the two integrals in (23) for obtaining $\tilde{P}_{n\kappa}(r)$ and $\tilde{Q}_{n\kappa}(r)$, respectively, as a function of r . As default in XGREENS, we use the *overlap* integral

$$\int \left(\tilde{P}_{n\kappa}(r) P_{n\kappa}(r) + \tilde{Q}_{n\kappa}(r) Q_{n\kappa}(r) \right) dr \quad (26)$$

for the two lowest principal quantum numbers n of the (given) symmetry κ , together with the corresponding *normalization* integral

$$\int \left(\tilde{P}_{n\kappa}(r) \tilde{P}_{n\kappa}(r) + \tilde{Q}_{n\kappa}(r) \tilde{Q}_{n\kappa}(r) \right) dr, \quad (27)$$

as a *numerical measure* on the accuracy of the generated Green's functions. These integrals are displayed explicitly by the program (on demand). For a standard (logarithmic) grid with about 300 nodes, the overlap integral (26) is typically within the range $10^{-2} \dots 10^{-3}$. For such a grid, the accuracy is limited in the computations by the linear interpolation of the wave and Green's functions. The accuracy can be increased however for a larger number i_{\max} of grid points as shown in section 4.

3 Program structure

3.1 The RATIP package

Similar as GRASP92 [9] was designed for generating the wave functions within the multi-configuration Dirac-Fock (MCDF) model, the RATIP package [19, 20, 21] is organized as a

suite of program components to calculate a variety of (relativistic) atomic transition and ionization properties. Among other features, the components of RATIP support for instance investigations on the autoionization of atoms and ions, the interaction with the radiation field, the parametrization of angular distributions in the emission of electrons and photons, or the analysis of interference effects between radiative and non-radiative processes. In quite different case studies, RATIP has helped analyze and interpret a large number of spectra and experiments. In order to provide efficient tools for atomic computations, it also incorporates a number of further components (beside of the main program components for calculating certain physical properties) which facilitate the transformation of wave functions between different coupling schemes or the generation of continuum orbitals and angular coefficients. With the development of the XGREENS program, we now provide an additional component to generate the relativistic central-field Green's functions within the RATIP environment. This is rather independent of their later 'use' where different properties such as the two-photon ionization and decay or various polarizabilities of atoms and ions might be calculated with the help of these functions. Owing to the large number of possible applications, however, a support of certain properties will largely depend on the requests by the users and on our further experience with the code.

Not much more need to be said about RATIP's overall structure. A detailed account on its present capabilities has been given previously [22]. With regard to the further development of RATIP, we just note that our main concern now pertains to a long life-cycle of the code and to an object-oriented design within the framework of Fortran 90/95. With the present set-up of the XGREENS component, we continue our effort for providing an atomic code which is prepared for future applications in dealing with open-shell atoms and ions.

3.2 Data structures and program execution

Certainly, the major purpose of XGREENS is the computation of (one-electron) radial Green's functions for some — specified or externally given — central-field potential, which can later be utilized for calculating radial matrix elements of the type

$$U_{\beta\kappa\alpha}^{T_{\beta}T_{\kappa}T_{\alpha}}(k, \Lambda; E; \tilde{k}, \tilde{\Lambda}) = \int \int_0^{\infty} g_{\beta}^{T_{\beta}}(r) j_{\Lambda}(kr) g_{E\kappa}^{T_{\kappa}}(r, r') j_{\tilde{\Lambda}}(\tilde{k}r') g_{\alpha}^{T_{\alpha}}(r') dr dr', \quad (28)$$

where $j_{\Lambda}(kr)$ denotes a spherical Bessel function, $g_{E\kappa}^{T_{\kappa}}(r, r')$ one of the components of the radial Green's function in (4), and where α and β refer to the radial wave functions of some bound or free-electron state, respectively. Matrix elements of this type play a key role, for instance, for studying two-photon ionization (bound-free) or decay (bound-bound) processes. Since the (four) components of the radial Green's functions depend on two radial coordinates, r and r' , a rather large amount of data need usually to be calculated by means of XGREENS. These data are finally stored in an external (`.rgf`) radial Green's function file as will be discussed in the next subsection.

To generate and utilize the Green's functions, two derived data types `TGreens_single_rgf` and `TGreens_rgf` have been introduced as shown in Figure 1. Using these data types, a single Green's function is kept internally in terms of its expansion coefficients from Eqs. (11) and (12) for the *large-large* and a similar set of coefficients for the *small-small* component on the given grid. Apart from the particular representation of the grid, these data structures contain

```

type :: TGreens_single_rgf
-----
! Data structure type to keep a single Green's function
-----
  real(dp)                :: energy
  integer                 :: kappa
  ! Coefficients for the regular and irregular solutions
  real(dp), dimension(:, :), allocatable :: fLL1, fLL2, fSS1, fSS2
  ! Values of the regular and irregular solutions and their derivatives
  real(dp), dimension(:), allocatable   :: mL, wL, mS, wS, &
                                          mLp, wLp, mSp, wSp
end type TGreens_single_rgf
!
!
type :: TGreens_rgf
-----
! Data structure type to save the Green's functions
-----
  type(TGreens_single_rgf), dimension(:), allocatable :: gf
  integer                 :: interpolation_mode, mtp
  real(dp), dimension(:), allocatable :: yp, z0, z1
end type TGreens_rgf

```

Figure 1: The derived data structures `TGreens_single_rgf` and `TGreens_rgf` to generate, store, and interpolate a central-field Green's function.

the energy and symmetry of the radial Green's function, the nuclear charge function(s) as well as information about the mode of interpolation of the radial components between the grid points and the maximum tabulation point `mtp`. In `XGREENS`, a variable of `type(TGreens_rgf)` is used in order to store the information about all the requested functions, and a few additional procedures are provided to calculate from these structures the values of the radial components for any set of arguments.

The basic steps in the execution of the program are very similar as for other components of the `RATIP` package. At the beginning, all the necessary input data are read in by an (interactive) dialog. The requested Green's functions are then calculated in turn and tested for their accuracy. The (main) output of the program is a formatted ASCII file which provides an interface for further applications, either within the `RATIP` environment or as worked out by the user.

3.3 Interactive control and output of the program

Like the other components of the `RATIP` package, `XGREENS` is controlled by a dialog at the beginning of the execution. In this dialog, all information need to be specified for obtaining the central-field potential as well as about the number and symmetry of the radial Green's functions to be generated. Owing to various choices for defining the spherical potential, however, slightly different dialogs may occur during the execution. An example is shown in Figure 2, where first a Hartree-plus-statistical-exchange (HX) potential due to Cowan [23, 24] is generated from the ground-state wave functions of atomic gold, and then two radial Green's functions are calculated within this potential.

Apart from the nuclear charge, given in terms of a `GRASP92 .iso` isotope data file, the dialog first prompts for specifying (or confirming) some basic parameters such as the speed of light, the grid parameters as well as for the energy units, in which the further input and output is done by the program. This is followed by a prompt for determining the central-field potential for the radial Green's functions. At present, `XGREENS` supports four models including a pure

Coulomb potential (for the calculation of Coulomb Green's functions) as well two potentials (HFS and HX) to incorporate also the *exchange interaction* in some approximate form. In the **Hartree** model, in contrast, only the *direct* potential of some atomic level is applied in the later computation of the Green's functions. In all these cases, however, the wave functions of the selected state have to be specified in terms of the corresponding GRASP92 files for the configuration state functions (CSF), mixing coefficients as well as the radial orbitals. If computed internally, the potential can be written also to disc and used in further applications. Beside of the internal set-up of the potential, in addition, a user-defined potential can be given also explicitly and *read in* by the program.

Although the nuclear charge is specified by means of a `.iso` file (in line with all other components of RATIP), the Green's functions are always generated for a *point-like* nucleus in order to 'utilize' their regular behaviour of the radial components at the origin [cf. section 2.2]. For each radial Green's function, then the energy and the one-particle symmetry κ need to be specified. The functions are finally written to the `.rgf` radial Green's function file whose name has also to be given at the end of the dialog. In this file, the radial Green's functions are given at the grid (in r and r') as specified originally. Moreover, to test the accuracy of the Green's functions, a number of overlap and normalization integrals are calculated on request in order to 'compare' a few low-lying orbitals, as obtained from the Green's functions by an integration over r' , with independently generated functions from Salvat's program [10]. In average, the computation of a single Green's function requires about 2 min on a 450 MHz Pentium PC and approximately the same time for the 'test' integrals. In the latter case, the rather large demand on CPU time arises mainly from the $2i_{\max}$ radial integrals in r' -space, which need first to be performed in order to obtain the radial orbital functions from the given Green's function components.

3.4 Distribution and installation

A program of RATIP's size cannot be maintained over a longer period without that certain changes and the adaptation of the code to recent developments (in either the hardware or the operating systems) become necessary from time to time. For the distribution of the code, therefore, we follow our previous style in that the RATIP package is provided as whole. The main emphasis with the present extension of the program, however, is placed on the design and implementation of the two (new) modules `rabs_greens.f90` and `rabs_utilities_2.f90` which contain the code for the generation and the test of the radial Green's functions. In addition, the four modules (`rabs_special_functions.f90`, `rabs_error_control.f90`, `rabs_greens_external.f90`, and `rabs_cpc_salvat_1995.f`) became necessary and had to be appended to the code in order to support an accurate computation of the hypergeometric and a few related functions from mathematical physics as well as for providing Salvat's solver [10] for the generation of the radial wave functions ($P(r)$, $Q(r)$) within a given potential.

In the present version, the RATIP package now contains the source code for the 8 components ANCO, CESD, LSJ, GREENS, RCFP, RELCI, REOS as well as the UTILITIES for performing a number of small but frequently occurring tasks. Together with the six additional modules from above, the overall program therefore comprises about 40.000 lines of code, separated into 22 modules (apart from the main program components and three libraries). All these source files are provided in the `Ratip` root directory. As before, there is one *makefile* for each individual

component from which the corresponding executable can be obtained simply by typing the command `make -f make-component`, that is `make -f make-greens` in the present case. For most components of the RATIP package, in addition, we provide a test suite in a subdirectory `test-component` of the root where `component` refers to the names above. For example, the directory `test-greens` contains all the necessary files to run the sample calculations which we will discuss below.

Before, however, the makefiles can be 'utilized', a number of global variables need to be specified for the compilation and linkage of the program. In a LINUX or UNIX environment, this is achieved by modifying (and *sourcing*) the script file `make-environment` which saves the user from adopting each makefile independently. In fact, the script `make-environment` just contains a very few lines for specifying the local compiler, the options for the compiler, as well as the local paths for the libraries. Under WINDOWS, in contrast, not much help need to be given to the user since most compiler nowadays provide the feature to define 'projects'. In this case, it is recommended to *read off* the required modules and source files from the makefile of the program component and to 'declare' them directly to the project as associated with the given component.

In the past year, the XGREENS program has been applied under several LINUX systems using the LAHEY Fortran 95 compiler. The RATIP program as a whole has been found also portable rather easily to other platforms such as IBM RS/6000, SUN OS, or to the PC world. The file `Read.me` file in the `ratip` root directory contains further details for the installation. Overall, however, it is expected that it will not be difficult to compile the program also under other operating systems.

4 Test calculations

To illustrate the use of the XGREENS program, we briefly discuss and display two examples. They refer to the generation of the radial Green's function for a few selected (one-electron) symmetries in atomic gold ($Z = 79$) and demonstrate how the accuracy of these functions can be increased by a proper choice of the radial grid. However, before the radial components can be generated, we need first to specify the potential as shown in Figure 2. For the present examples, we have chosen a HX (Hartree-plus-statistical-exchange) due to the work of Cowan [23, 24], starting from the ground-state wave functions of neutral gold. As usual for GRASP92 and RATIP, these wave functions have to be provided in terms of the `.csl` configuration state list and the `.mix` configuration mixing files as well as the `.out` radial orbital file. All of these input files are provided also in the `test-greens/` subdirectory of the `Ratip` root directory and, thus, can be used for the present tests. In Figure 2 moreover, the potential is saved to the central-field potential file `z79-au-hx.pot` and later re-utilized in Figure 3. The output of the two examples are shown in the TEST RUN OUTPUT below.

Like for the wave functions, the 'quality' of the generated Green's functions becomes only fully apparent, if they are used for calculating *observables* which can be compared to experiment. Although calculation of observables is not the aim of the present work, it is still possible to test the accuracy of the generated Green's functions by re-calculating the radial orbitals (as discussed in section 2.3) and by comparing these orbitals with those as obtained from the integration of the Dirac equation for the given central field. This 'comparison' is done in XGREENS

```

XGREENS: Calculation of relativistic central-field Green's functions
with energies E < 0 (Fortran 95 version);
(C) Copyright by P Koval and S Fritzsche, Kassel (2004).

Enter a file name for the greens.sum file:
z79-au-pot.sum
Enter the name of the isotope data file:
z79.iso
loading isotope data file ...
... load complete;
The physical speed of light in atomic units is 137.0359895000000 ;
revise this value ?
n
The parameters of the radial grid 1 (first grid) are
rnt = 2.177968408335618E-04 ;
h = 6.250000000000000E-02 ;
hp = 0.000000000000000E+00 ;
n = 390 ;
revise these values ?
n
Which units are to be used to enter and to print the energies:
A : Angstrom;
eV : electron volts;
Hartree : Hartree atomic units;
Hz : Hertz;
Kayser : [cm**(-1)];
eV
Determine type of central-field potential to generate:
Load : Load a potential from a .pot file
Coulomb : (pure) Coulomb potential
Hartree : Direct potential for a given ASF
HFS : Hartree-Fock-Slater method
HX : Hartree-plus-statistical-eXchange (Cowan 1967)
HX
Enter the name of the .csl (configuration states list) file:
au.csl
Loading configuration symmetry list file ...
There are 22 relativistic subshells;
there are 3 relativistic CSFs;
... load complete.
Enter the name of the GRASP92 mixing coefficient file:
z79-au.mix
Loading mixing coefficients file ...
... load complete;
Enter the name of the rwf data file:
z79-au.rwf
... load complete;
Summary of all ASF to facilitate the selection of proper bound-state levels

  i  Level  J^P  Energy (a.u.)  Energy (eV)
-----
  1  1  1/2 +  -1.90397E+04  -5.18096E+05

Enter ASF level number for which the potential should be calculated:
1
Enter the subshell (e.g. 1s, 2p-, ...) which is specific to Cowan's HX method:
1s
Write the generated potential to disc ?
y
Enter the name of .pot central-field potential file:
z79-au-hx.pot
Radial Green's functions will be calculated within the range 0 <= r, r' <= 4.797 a.u.
with the boundaries of the nuclear charge function Z(0) = 79.00 and Z(r_max) = 1.951
In the given potential the one-electron energies (in eV) are:
1s: -8.131E+04
2s: -1.453E+04  2p-: -1.402E+04  2p: -1.214E+04
3s: -3.479E+03  3p-: -3.232E+03  3p: -2.814E+03  3d-: -2.382E+03  3d: -2.289E+03

Enter in turn the energies E (in eV) and symmetries of the radial Green's functions to be generated;
Enter another energy and symmetry (<cr> if done):
-10000 s
Enter another energy and symmetry (<cr> if done):
-15000 d-
Enter another energy and symmetry (<cr> if done):

Check the accuracy of the Green's functions after generation ?
y
Enter the name of .rgf file to save the Green's function:
z79-au-pot.rgf
.
.

```

Figure 2: Interactive dialog for calculating the effective potential and for generating the radial Green's functions.

```

.
.
The parameters of the radial grid 1 (first grid) are
  rnt = 2.177968408335618E-04 ;
  h   = 6.250000000000000E-02 ;
  hp  = 0.000000000000000E+00 ;
  n   = 390 ;
  revise these values ?
y
Enter rnt:
2.177968408335618E-04
Enter h:
3.125E-2
enter hp:
0
enter n:
780
Which units are to be used to enter and to print the energies:
  A      : Angstrom;
  eV     : electron volts;
  Hartree : Hartree atomic units;
  Hz     : Hertz;
  Kayser  : [cm**(-1)];
eV
Determine type of central-field potential to generate:
  Load   : Load a potential from a .pot file
  Coulomb : (pure) Coulomb potential
  Hartree : Direct potential for a given ASF
  HFS     : Hartree-Fock-Slater method
  HX      : Hartree-plus-statistical-eXchange (Cowan 1967)
Load
Enter the name of a .pot file with a central-field potential
z79-au-hx.fld
Radial Green's functions will be calculated within the range 0 <= r, r' <= 5.269 a.u.
with the boundaries of the nuclear charge function Z(0) = 79.00 and Z(r_max) = 1.000
In the given potential the one-electron energies (in eV) are:
  1s: -8.131E+04
  2s: -1.453E+04  2p-: -1.402E+04  2p: -1.214E+04
  3s: -3.479E+03  3p-: -3.232E+03  3p: -2.814E+03  3d-: -2.382E+03  3d: -2.290E+03

Enter in turn the energies E (in eV) and symmetries of the radial Green's functions to be generated;
Enter another energy and symmetry (<cr> if done):
-1000 s
Enter another energy and symmetry (<cr> if done):
-10000 s
Enter another energy and symmetry (<cr> if done):
-15000 p
Enter another energy and symmetry (<cr> if done):
-10000 p-
Enter another energy and symmetry (<cr> if done):
-15000 d-
Enter another energy and symmetry (<cr> if done):
-10000 d
Enter another energy and symmetry (<cr> if done):

Check the accuracy of the Green's functions after generation ?
y
Enter the name of .rgf file to save the Green's function:
z79-au-rgf.rgf
.
.

```

Figure 3: Dialog for calculating the radial Green's functions with an increased number of radial points.

on request by evaluating for the two lowest principal quantum numbers n the (radial) overlap integrals of the re-calculated functions with the solutions by Salvat's program. In addition, the *normalization* integrals are also displayed as seen from the TEST RUN OUTPUT. Except of a few cases, the deviation of these integrals from 1.0 are typically well below 0.1 % on the standard grid with about 300 mesh points in r and r' . For these deviations, there are two source of numerical 'inaccuracy' which arise from the test procedure and are not related to the generation of the radial Green's functions. They are caused by the fact that by using Salvat's solver [10], a third-order spline is used to represent the potential at intermediate points in r in contrast to the linear representation (9) for the generation of the Green's functions. Moreover, the integration of the radial integrals uses the standard GRASP92 procedure and, hence, is not adapted as well to Salvat's solutions.

The accuracy of the Green's functions (and the test integrals) can be improved however if the number of grid is enlarged, i. e. the spacing between the mesh points reduced. In our second example, cf. Figure 3, we therefore adopt a grid with approximately twice the number of mesh points. Note that this requires four times as much storage as the radial components are functions in r and r' . In this test case, moreover, the radial Green's functions are generated for four different symmetries s , $p_{1/2}$, $p_{3/2}$, $d_{3/2}$, and $d_{5/2}$. When the TEST RUN OUTPUT from this example is compared with those from example 1, we see that the accuracy in the overlap integrals is increased by about a factor of 5. For this example, the generation and test took about 30 minutes in total on a 450 MHz Pentium III.

After the termination of XGREENS, the radial Green's functions file (e. g. `z79-au-rgf.rgf` from example 2) contains all the Green's function components which were generated during the execution. Since this is a formatted file, it can easily be read and manipulated by any text editor. This (radial Green's function) file stores the individual components $g_{E\kappa}^{TT'}(r, r')$ of the Green's functions as 2-dimensional arrays within a simple file structure. An (internal) file signature `# DCFGF` in the first line is followed by the mode of interpolation and the number of Green's functions which are provided by the file. Then, each Green's function is specified (in turn), starting with the energy and symmetry of the function and followed by a table of six rows where the first two rows refer to the coordinates r and r' (in atomic units) and the other rows to the four component functions $g_{E\kappa}^{LL}(r, r')$, $g_{E\kappa}^{LS}(r, r')$, $g_{E\kappa}^{SL}(r, r')$ and $g_{E\kappa}^{SS}(r, r')$ in this particular order. Although this format is convenient for the later use of these functions, it may lead to rather large data files, especially if some larger number of Greens' functions need to be generated. In practise, however, not much problems are expected with this file structure because disc storage became cheap recently and because, for most applications, we expect the Green's functions to be generated *on demand* by making use of the corresponding modules instead of keeping them in external files. Typically, the radial wave and Green's functions occur as part of matrix elements and, thus, first require an additional integration (over r and/or r') before any *observable* quantity is obtained.

The format of the radial Green's function (`.rgf`) file can be used easily in order to plot the various radial components. In Figure 4, therefore, we display the nuclear charge function $Z(r)$ and the two radial Green's function components $g_{E_s}^{LL}(r_0, r)$ and $g_{E_s}^{SL}(r_0, r)$ as function of (second) argument r and taken for $r_0 = 0.204076$ a. u. The radial Green's functions are calculated in the ground-state potential of atomic gold, as applied in example 2, for the energy $E = 1000$ eV. As seen from Figure 4, the *large-large* component $g_{E_s}^{LL}$ is continuous at $r = r'$ while the *small-large* component $g_{E_s}^{SL}$ jumps owing to Eqs. (20) and (21) at this position

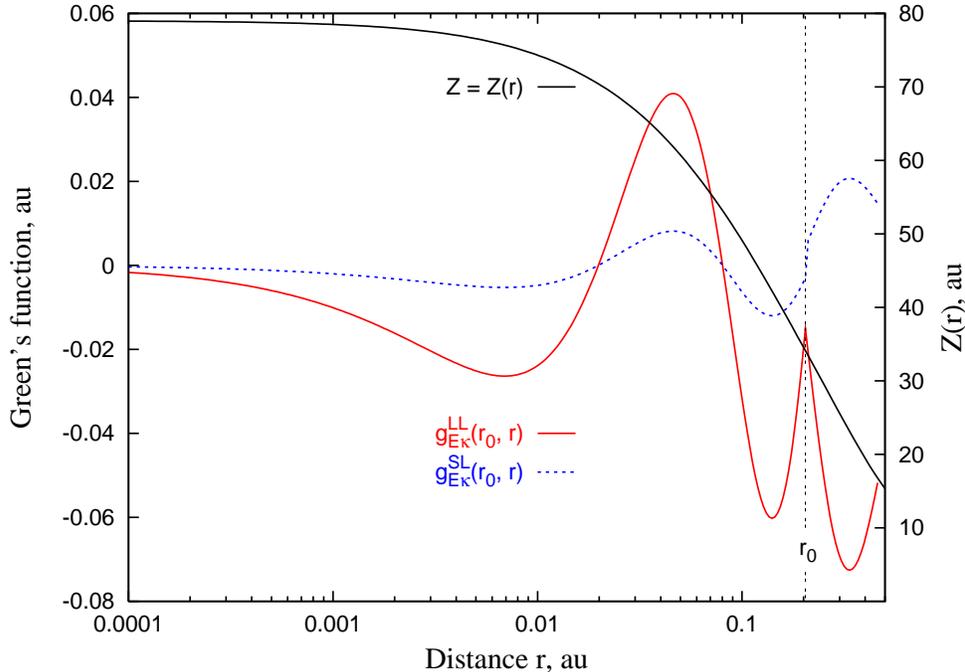


Figure 4: Nuclear charge $Z = Z(r)$ and the radial Green's function components $g_{E\kappa}^{LL}(r_0, r)$ and $g_{E\kappa}^{SL}(r_0, r)$ as function of r and for $r_0 = 0.204076$ a.u. The radial Green's functions with s -symmetry ($\kappa = -1$) are calculated in the ground-state potential of atomic gold for the energy $E = 1000$ eV.

in space. Both components, moreover, behave 'regularly' at the origin as was constructed explicitly by Eq. (8).

5 Outlook. Applications of central-field Green's functions

Apart from fundamental interest in having the central-field Green's functions available for 'relativistic' electrons, these functions are also useful for the perturbative treatment of atoms and ions. As discussed in subsection 2.3, namely, the Green's function provide a simple access to the complete spectrum of a quantum system and, hence, can be utilized for carrying out the summation over all the (one-particle) states of the spectrum as required in second- and higher-order perturbation theory. However, since we only provide the *one-electron* Green's functions, they can be applied for just those processes where the 'perturbations' are described in terms of one-particle operators. Perhaps, the most-studied perturbation of this type is the interaction of atoms and ions with the radiation field, which — within a sufficiently strong field — may lead not only to atomic photoionization but (in second order) also to the two-photon ionization and decay of atoms and ions and to several other processes. During the last two years, we utilized the central-field Green's functions mainly for exploring the two-photon ionization for the helium-like ions and for the inner-shell electrons from atomic neon and argon.

Apart from the one-particle Green's functions (as discussed in this work), there are a number of further processes such as the double Auger decay, for which the *two-particle* Green's functions $G_E(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2)$ are required in order to calculate the cross sections, decay rates and/or angular distributions. These two-particle functions are solutions to a *defining equation* similar to Eq. (2) but where the (one-particle) Dirac Hamiltonian \hat{H}_D is replaced by the two-

particle operator $\hat{H}_{D,1} + \hat{H}_{D,2} + \hat{V}_{12}$, including the electron–electron interaction \hat{V}_{12} explicitly. Even by making use of a proper *radial–angular* decomposition of such Green’s functions, their radial part $g_{\kappa_1, \kappa_2}^k(r_1, r_2; r'_1, r'_2)$ would depend then on four radial variables and an overall rank k , similar as known from the tensorial decomposition of the electron–electron interaction [25]. Therefore, an internal representation and generation of these (radial) functions appear rather infeasible in practise. An alternative to these two–particle Green’s functions is given by the (so–called) *modified pair functions* $\Phi_{E,\alpha}(\mathbf{r}_1, \mathbf{r}_2)$ which satisfy the equation

$$\left\{ \hat{H}_{D,1} + \hat{H}_{D,2} + \hat{V}_{12} - E \right\} \Phi_{E,\alpha}(\mathbf{r}_1, \mathbf{r}_2) = \hat{W} |\Psi_\alpha(PJM)\rangle ,$$

where \hat{W} is a one– or two–particle operator which depends on the physical task to be solved and $|\Psi_\alpha(PJM)\rangle$ is one of the (two–electron) solutions of the corresponding homogeneous equation. These modified pair functions have the advantage that they only depend on two radial variables similar as the one–particle Green’s functions. On the other hand, of course, these functions now depend on some (initial) two–particle state $|\Psi_\alpha(PJM)\rangle$ as well as on the particular choice of the interaction operator \hat{W} and, hence, are less general when compared with the Green’s function from above. We currently investigate the possibilities for generating also such modified pair functions within the framework of RATIP and for their (later) use in the description of the double Auger decay. But already the one–particle Green’s functions from this work enables one to explore a number of atomic properties which have not been studied before for complex atoms or, at least, not within a relativistic framework.

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TEST RUN OUTPUT

 ** Example 1 **

Generation of radial Green's functions

i	E (eV)	j	overall progress
1	-1.000000E+04	s	50%
2	-1.500000E+04	d-	100%

Tests on the accuracy of the Green's functions by means of overlap and normalization integrals:

i	E (eV)	nj	Overlap integrals		Normalization
			<nj (Greens) nj (Salvat 95)>	nj (Greens)	
1	-1.000000E+04	1s	1.000020E+00	1.000057E+00	
1	-1.000000E+04	2s	1.001925E+00	1.003888E+00	
2	-1.500000E+04	3d-	9.997536E-01	9.995404E-01	
2	-1.500000E+04	4d-	1.005937E+00	1.012284E+00	

Write the Green's functions to the .rgf file;
 2 radial Green's functions with 5065446 bytes ...

XGREENS complete ...

 ** Example 2 **

Generation of radial Green's functions

i	E (eV)	j	overall progress
1	-1.000000E+03	s	16%
2	-1.000000E+04	s	33%
3	-1.500000E+04	p	50%
4	-1.000000E+04	p-	66%
5	-1.500000E+04	d-	83%
6	-1.000000E+04	d	100%

Tests on the accuracy of the Green's functions by means of overlap and normalization integrals:

i	E (eV)	nj	Overlap integrals		Normalization
			<nj (Greens) nj (Salvat 95)>	nj (Greens)	
1	-1.000000E+03	1s	1.000267E+00	1.000540E+00	
1	-1.000000E+03	2s	1.000318E+00	1.000641E+00	
2	-1.000000E+04	1s	1.000003E+00	1.000010E+00	
2	-1.000000E+04	2s	1.000138E+00	1.000278E+00	
3	-1.500000E+04	2p	9.993563E-01	9.987343E-01	
3	-1.500000E+04	3p	9.999064E-01	9.998404E-01	
4	-1.000000E+04	2p-	1.000384E+00	1.000770E+00	
4	-1.000000E+04	3p-	1.000216E+00	1.000435E+00	
5	-1.500000E+04	3d-	1.000046E+00	1.000107E+00	
5	-1.500000E+04	4d-	1.001539E+00	1.003181E+00	
6	-1.000000E+04	3d	1.000084E+00	1.000173E+00	
6	-1.000000E+04	4d	1.001030E+00	1.002106E+00	

Write the Green's functions to the .rgf file;
 6 radial Green's functions with 59754187 bytes ...

XGREENS complete ...

Relativistic central-field Green's functions for the RATIP package

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Abstract

From perturbation theory, Green's functions are known for providing a simple and convenient access to the (complete) spectrum of atoms and ions. Having these functions available, they may help carry out perturbation expansions to any order beyond the first one. For most realistic potentials, however, the Green's functions need to be calculated numerically since an analytic form is known only for *free* electrons or for their motion in a pure Coulomb field. Therefore, in order to facilitate the use of Green's functions also for atoms and ions other than the hydrogen-like ions, here we provide an extension to the RATIP program which supports the computation of relativistic (one-electron) Green's functions in an — arbitrarily given — central-field potential $V(r)$. Different computational modes have been implemented to define these effective potentials and to generate the radial Green's functions for all bound-state energies $E < 0$. In addition, care has been taken to provide a user-friendly component of the RATIP package by utilizing features of the Fortran 90/95 standard such as data structures, allocatable arrays, or a module-oriented design.

PROGRAM SUMMARY

Title of program: XGREENS.

Catalogue number: To be assigned.

Program obtainable from: CPC Program Library, Queen's University of Belfast, N. Ireland. Users may also down-load a tar-file of the program `ratip00.tar` from our home page at the University of Kassel (<http://www.physik.uni-kassel.de/fritzsche/programs.html>).

Licensing provisions: None.

Computer for which the new version has been tested: PC Pentium II, III, IV, Athlon.

Installations: University of Kassel (Germany).

Operating systems: SuSE Linux 8.2, SuSE Linux 9.0.

Program language used in the new version: ANSI standard Fortran 90/95.

Memory required to execute with typical data: On a standard grid (400 nodes), one central-field Green's function requires about 50 kBytes in RAM while approximately 3 MBytes are needed if saved as two-dimensional array on some external disc space.

No. of bits in a word: Real variables of double- and quad-precision are used.

Peripheral used: Disk for input/output.

CPU time required to execute test data: 2 minutes on a 450 MHz Pentium III processor.

Distribution format: compressed tar file.

Keywords: Central-field Green's function, confluent hypergeometric function, Coulomb Green's function, Kummer function, multi-configuration Dirac-Fock, regular and irregular solutions.

Nature of the physical problem: In atomic perturbation theory, Green's functions may help carry out the summation over the complete spectrum of atom and ions, including the (summation over the) bound states as well as an integration over the continuum [1]. Analytically, however, these functions are known only for *free* electrons ($V(r) \equiv 0$) and for electrons in a *pure* Coulomb field ($V(r) = -Z/r$). For all other choices of the potential, in contrast, the Green's functions must be determined numerically.

Method of solution: Relativistic Green's functions are generated for an arbitrary central-field potential $V(r) = -Z(r)/r$ by using a piecewise linear approximation of the effective nuclear charge function $Z(r)$ on some grid r_i ($i = 1, \dots, N$): $Z_i(r) = Z_{0i} + Z_{1i}r$. Then, following McGuire's algorithm [2], the radial Green's functions are constructed from the (two) linear-independent solutions of the homogeneous equation [3]. In the computation of these radial functions, the Kummer and Tricomi functions [4] are used extensively.

Restrictions onto the complexity of the problem: The main restrictions of the program concern the shape of the effective nuclear charge $Z(r) = -rV(r)$, i. e. the choice of the potential,

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and the allowed energies. Apart from obeying the proper boundary conditions for a point-like nucleus, namely, $Z(r \rightarrow 0) = Z_{\text{nuc}} > 0$ and $Z(r \rightarrow \infty) = Z_{\text{nuc}} - N_{\text{electrons}} \geq 0$, the first derivative of the charge function $Z(r)$ must be smaller than the (absolute value of the) energy of the Green's function, $\frac{\partial Z(r)}{\partial r} < |E|$.

Unusual features of the program: XGREENS has been designed as a part of the RATIP package [5] for the calculation of relativistic atomic transition and ionization properties. In a short dialog at the beginning of the execution, the user can specify the choice of the potential as well as the energies and the symmetries of the radial Green's functions to be calculated. Apart from central-field Green's functions, of course, the Coulomb Green's function [6] can also be computed by selecting a constant nuclear charge $Z(r) = Z_{\text{eff}}$. In order to test the generated Green's functions, moreover, we compare the two lowest bound-state orbitals which are calculated from the Green's functions with those as generated separately for the given potential. Like the other components of the RATIP package, XGREENS makes careful use of the Fortran 90/95 standard.

References:

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LONG WRITE-UP

1 Introduction

The use of Green's function has a long tradition for solving physical problems, both in classical and quantum physics. From perturbation theory, for instance, these functions are known for providing a rather simple access to the complete spectrum of a quantum system and, hence, to facilitate the computation of perturbation expansions beyond the first order in perturbation theory. Applications of the Green's functions can be therefore found not only in atomic and molecular physics but also in quantum optics, field theory, solid-state physics, and at various place elsewhere.

In atomic physics, however, the use of Green's function methods was so far mainly restricted to describe the motion of electrons in a pure Coulomb field, i. e. to the theory of hydrogen and hydrogen-like ions. For these one-electron systems, calculations have been carried out, for example, for the two-photon [1, 2] and multi-photon ionization [3, 4], the two-photon decay [5], the second-order contributions to the atomic polarizabilities [6] as well as for determining radiative corrections [7, 8].

Less attention, in contrast, has been paid to utilize Green's functions for non-Coulomb fields or for describing the properties of many-electron atoms and ions. Unlike to the generation of the — bound and free-electron — wave functions to the Schrödinger and Dirac equation, for which a number of programs are available now also within the CPC-library [9, 10], there is almost no code freely available which helps generate the relativistic central-field Green's functions. As known from the literature, however, nonrelativistic central-field Green's functions were constructed by McGuire [11] and by Huillier and coworkers [12], and were successfully applied for studying the multi-photon ionization of valence-shell electrons in alkali atoms. Therefore, in order to facilitate the use of relativistic central-field Green's functions for atomic computations, here we describe and provide an extension to the RATIP package which calculates these functions (as the solution of the Dirac equation with a δ -like inhomogeneity) for an arbitrary central field $V(r)$.

In the following section, we start with summarizing the basic formulas for the computation of relativistic central-field Green's functions. Apart from a brief discussion of the Dirac Hamiltonian, this includes the *defining equation* for central-field Green's function and the separation of the three-dimensional Green's function into radial and angular parts. However, since the separation has been discussed in detail elsewhere in the literature [13], we restrict ourselves to a short account on that topic and mainly focus on the computation of the radial components of the Green's functions. Section 3 later describes the program structure of XGREENS, its interactive control and how the code is distributed. Because the XGREENS program is designed as part of the RATIP package, we have used and modified several modules which were published before along with other components of the program. Section 4 explains and displays two examples of XGREENS, including (a) a dialog in order to calculate a central-field potential from GRASP92 wave functions [9] and (b) the generation of the radial Green's functions if the potential is loaded from an external file. Finally, a short summary and outlook is given in section 5.

2 Theoretical background

2.1 Relativistic central-field Green's functions

Most naturally, the relativistic central-field Green's function can be considered as a generalization of the (relativistic) Coulomb Green's function if, in the Dirac Hamiltonian¹

$$\hat{H}_D(\mathbf{r}) = -i\mathbf{c}\boldsymbol{\alpha}\nabla + \beta c^2 + V(r), \quad (1)$$

the Coulomb potential is replaced by some (arbitrarily given) central-field potential, $V^C(r) = -\frac{Z}{r} \rightarrow -\frac{Z(r)}{r}$. As in the nonrelativistic case where the Green's function obeys the *defining* equation $(\hat{H} - E)G_E(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}')$, the relativistic Green's function is given by a 4×4 matrix [14] which satisfies the inhomogeneous equation

$$\left(\hat{H}_D(\mathbf{r}) - E - c^2\right) G_E(\mathbf{r}, \mathbf{r}') = \delta(\mathbf{r} - \mathbf{r}') \mathbf{I}_4, \quad (2)$$

with \mathbf{I}_4 being the 4×4 unit-matrix and where, as usual in atomic structure theory, E refers to the total energy of the electron but without its rest energy $m_e c^2$. Moreover, since in polar coordinates a central-field potential $Z(r)$ in the Hamiltonian (1) does not affect the separation of the variables, the central-field Green's function has the same *radial-angular* representation as in the pure Coulomb case [13]

$$G_E(\mathbf{r}, \mathbf{r}') = \sum_{\kappa m} \frac{1}{rr'} \begin{pmatrix} g_{E\kappa}^{LL}(r, r') \Omega_{\kappa m}(\hat{\mathbf{r}}) \Omega_{\kappa m}^\dagger(\hat{\mathbf{r}}') & -i g_{E\kappa}^{LS}(r, r') \Omega_{\kappa m}(\hat{\mathbf{r}}) \Omega_{-\kappa m}^\dagger(\hat{\mathbf{r}}') \\ i g_{E\kappa}^{SL}(r, r') \Omega_{-\kappa m}(\hat{\mathbf{r}}) \Omega_{\kappa m}^\dagger(\hat{\mathbf{r}}') & g_{E\kappa}^{SS}(r, r') \Omega_{-\kappa m}(\hat{\mathbf{r}}) \Omega_{-\kappa m}^\dagger(\hat{\mathbf{r}}') \end{pmatrix}, \quad (3)$$

where $\Omega_{\kappa m}(\hat{\mathbf{r}}) = \Omega_{\kappa m}(\vartheta, \varphi)$ denotes a standard spherical Dirac-spinor and $\kappa = \pm(j + 1/2)$ for $l = j \pm 1/2$ is the *relativistic* angular momentum quantum number; this number carries information about both the total angular momentum j as well as the parity $(-1)^l$ of the Green's function. While the summation over $\kappa = \pm 1, \pm 2, \dots$ runs over all (non-zero) integers, the summation over the magnetic quantum number $m = -j, -j + 1, \dots, j$ is restricted by the corresponding total angular momentum. Moreover, the radial part of the central-field Green's function $\begin{pmatrix} g_{E\kappa}^{LL}(r, r') & g_{E\kappa}^{LS}(r, r') \\ g_{E\kappa}^{SL}(r, r') & g_{E\kappa}^{SS}(r, r') \end{pmatrix}$ in (3) can be treated simply as a 2×2 matrix function which satisfies the equation

$$\begin{pmatrix} \left[-\frac{\alpha Z(r)}{r} - \alpha E\right] & \left[\frac{\kappa}{r} - \frac{\partial}{\partial r}\right] \\ \left[\frac{\partial}{\partial r} + \frac{\kappa}{r}\right] & \left[-\frac{2}{\alpha} - \frac{\alpha Z(r)}{r} - \alpha E\right] \end{pmatrix} \begin{pmatrix} g_{E\kappa}^{LL} & g_{E\kappa}^{LS} \\ g_{E\kappa}^{SL} & g_{E\kappa}^{SS} \end{pmatrix} = \alpha \delta(r - r') \mathbf{I}_2, \quad (4)$$

with \mathbf{I}_2 now being the 2×2 unit-matrix. Note that in Eq. (4), α refers to Sommerfeld's fine structure constant and that, in order to keep the equations similar to those for the Coulomb Green's functions [13], we make use of a nuclear charge function $Z(r) = -rV(r)$ to define the central-field potential, instead of $V(r)$ explicitly. In the radial-angular representation (3), two superscripts T and T' were introduced to denote the individual components in the 2×2 radial Green's function matrix. These superscripts take the values $T = L$ or $T = S$ to refer to

¹Here and in the following, we use atomic units ($m_e = \hbar = e^2/4\pi\epsilon_0 = 1$) if not stated otherwise.

either the *large* or *small* component, respectively, when multiplied with a corresponding (2-spinor) radial solution of the Dirac Hamiltonian (1). For a pure Coulomb potential, $Z(r) \equiv Z_{\text{eff}}$, an explicit representation of the (four) components $g_{E\kappa}^{TT'}(r, r')$ of the radial Green's function can be found in Refs. [13, 14, 15].

2.2 Generation of radial Green's functions

When compared with the Coulomb Green's functions, not much need to be changed for the central-field functions in Eqs. (3) and (4) except that the nuclear charge $Z = Z(r)$ now depends on r and, hence, that *analytic solutions* to these equations are no longer available. Therefore, to find a numerical solution to Eq. (4), let us first mention that this matrix equation just describes *coupled* equations for the two independent pairs $(g_{E\kappa}^{LL}, g_{E\kappa}^{SL})$ and $(g_{E\kappa}^{SS}, g_{E\kappa}^{LS})$ of the radial components. For example, if we consider the first pair $(g_{E\kappa}^{LL}, g_{E\kappa}^{SL})$ of radial components of the Green's function, it has to satisfy the two equations

$$\left[-\frac{\alpha Z(r)}{r} - \alpha E\right] g_{E\kappa}^{LL}(r, r') + \left[\frac{\kappa}{r} - \frac{\partial}{\partial r}\right] g_{E\kappa}^{SL}(r, r') = \alpha \delta(r - r'), \quad (5)$$

$$\left[\frac{\partial}{\partial r} + \frac{\kappa}{r}\right] g_{E\kappa}^{LL}(r, r') + \left[-\frac{2}{\alpha} - \frac{\alpha Z(r)}{r} - \alpha E\right] g_{E\kappa}^{SL}(r, r') = 0, \quad (6)$$

and a similar set of equations holds for the second pair $(g_{E\kappa}^{SS}, g_{E\kappa}^{LS})$. In the following, therefore, we will discuss the algorithm for solving Eqs. (5) and (6) but need not display the analogue formulas for the pair $(g_{E\kappa}^{SS}, g_{E\kappa}^{LS})$.

Inserting $g_{E\kappa}^{SL}(r, r')$ from Eq. (6) into (5), we arrive at the second-order inhomogeneous differential equation

$$\left(\frac{\partial}{\partial r} - \frac{\kappa}{r}\right) \frac{\left(\frac{\partial}{\partial r} + \frac{\kappa}{r}\right) g_{E\kappa}^{LL}(r, r')}{\frac{2}{\alpha} + \frac{\alpha Z(r)}{r} + \alpha E} + \left(\frac{\alpha Z(r)}{r} + \alpha E\right) g_{E\kappa}^{LL}(r, r') = \alpha \delta(r - r') \quad (7)$$

for the component $g_{E\kappa}^{LL}(r, r')$. Solution of this equation can be constructed as product of two linearly independent solutions [14]

$$g_{E\kappa}^{LL}(r, r') = M_{E\kappa}^{LL}(\min(r, r')) \cdot W_{E\kappa}^{LL}(\max(r, r')) \quad (8)$$

for the corresponding homogeneous case [cf. Eq. (10) below], where $M_{E\kappa}^{LL}(r)$ denotes a solution which is regular at the origin, and $W_{E\kappa}^{LL}(r)$ a solution regular at infinity. Below, we will obtain these functions following the numerical procedure as suggested by McGuire [11].

For this, let us start with approximating the nuclear charge function $Z(r)$ on some grid r_i , $i = 1, \dots, i_{\text{max}}$ in terms of a set of straight lines

$$Z_i(r) = Z_{0i} + Z_{1i} r, \quad \text{for } r_i \leq r \leq r_{i+1}, \quad (9)$$

and from the *homogeneous part* of Eq. (7)

$$\left(\frac{\partial}{\partial r} - \frac{\kappa}{r}\right) \frac{\left(\frac{\partial}{\partial r} + \frac{\kappa}{r}\right) g_{E\kappa}^i(r)}{\frac{2}{\alpha} + \frac{\alpha Z_i(r)}{r} + \alpha E} + \left(\frac{\alpha Z_i(r)}{r} + \alpha E\right) g_{E\kappa}^i(r) = 0 \quad (10)$$

as given for the i -th interval $[r_i, r_{i+1}]$ of the grid. In this Eq., we can drop the second argument r' in the component $g_{E\kappa}^{LL}$, since it now appears only as a parameter, and replace it by the superscript i to denote the particular piece of the grid for which we want the solution. From the approximation (9), moreover, we see that the nuclear charge function $Z_i(r)$ within the i -th interval gives rise to a *pure* Coulomb potential Z_{0i}/r and a constant which is simply *added* to the energy: $E \rightarrow Z_{0i} + E$. We therefore find that, within the given interval, the regular and irregular solutions at the origin in (8) can both be written as linear combinations of the corresponding solutions for a Coulomb field

$$M_{E\kappa}^i(r) = f_{i,1} M_{E\kappa}^{i,\text{Coulomb}}(r) + f_{i,2} W_{E\kappa}^{i,\text{Coulomb}}(r) \quad (11)$$

$$W_{E\kappa}^i(r) = g_{i,1} M_{E\kappa}^{i,\text{Coulomb}}(r) + g_{i,2} W_{E\kappa}^{i,\text{Coulomb}}(r) \quad (12)$$

with constants $\{f_{i,1}, f_{i,2}, g_{i,1}, g_{i,2}\}$ which still need to be determined. For the Coulomb potential, the functions $M_{E\kappa}^{i,\text{Coulomb}}(r)$ and $W_{E\kappa}^{i,\text{Coulomb}}(r)$ are known analytically and given by [14]

$$M_{E\kappa}^{i,\text{Coulomb}}(r) = r^{s_i} e^{-q_i r} [t_i M(-t_i + 1, 2s_i + 1, 2q_i r) + (\kappa - Z_{0i}/q_i) M(-t_i, 2s_i + 1, 2q_i r)], \quad (13)$$

$$W_{E\kappa}^{i,\text{Coulomb}}(r) = r^{s_i} e^{-q_i r} [(\kappa + Z_{0i}/q_i) U(-t_i + 1, 2s_i + 1, 2q_i r) + U(-t_i, 2s_i + 1, 2q_i r)], \quad (14)$$

where $M(a, b, r)$ and $U(a, b, r)$ denote the Kummer and Tricomi functions [16, 17], respectively, and where the quantities s_i , t_i and q_i are given by

$$s_i = \sqrt{\kappa^2 - \alpha^2 Z_{0i}^2}, \quad t_i = \frac{\alpha Z_{0i}((E + Z_{1i})\alpha^2 + 1)}{\sqrt{1 - ((E + Z_{1i})\alpha^2 + 1)^2}} - s_i, \quad (15)$$

$$q_i = \sqrt{-(E + Z_{1i})((E + Z_{1i})\alpha^2 + 2)}. \quad (16)$$

The set of constants $\{f_{i,1}, f_{i,2}, g_{i,1}, g_{i,2}; i = 1, \dots, i_{\max}\}$ can be determined from the fact that the two functions $M_{E\kappa}^{LL}(r)$ and $W_{E\kappa}^{LL}(r)$ in ansatz (8) as well as their derivatives need to be continuous in r , and that they behave *regularly* at the origin or at infinity, respectively. The constraint of being regular at the origin, for instance, requires the coefficients $f_{i=1,1} = 1$ and $f_{i=1,2} = 0$ and can be used together with the continuity $M_{E\kappa}^{LL}(r)$ and $M_{E\kappa}^{LLL}(r)$,

$$f_{i,1} M_{E\kappa}^{i,C}(r_i) + f_{i,2} W_{E\kappa}^{i,C}(r_i) = f_{i+1,1} M_{E\kappa}^{i+1,C}(r_i) + f_{i+1,2} W_{E\kappa}^{i+1,C}(r_i), \quad (17)$$

$$f_{i,1} M_{E\kappa}'^{i,C}(r_i) + f_{i,2} W_{E\kappa}'^{i,C}(r_i) = f_{i+1,1} M_{E\kappa}'^{i+1,C}(r_i) + f_{i+1,2} W_{E\kappa}'^{i+1,C}(r_i). \quad (18)$$

[where the superscript C here refers to the Coulomb functions in Eqs. (13) and (14)] in order to determine all the coefficients $f_{i,j}$ up to a normalization constant. A similar recurrence procedure also applies to the coefficients $g_{i,j}$, but by starting from 'infinity', that is with $g_{i_{\max},1} = 0$ and $g_{i_{\max},2} = 1$, and by going *backwards* in the index i towards the origin.

To determine finally the normalization of the radial component $g_{E\kappa}^{LL}(r, r')$, e. g. of the coefficients $\{f_{i,j}, g_{i,j}\}$, we may return to Eq. (7) and re-write it in the form

$$(\hat{h}_0 - E) g_{E\kappa}^{LL}(r, r') = \delta(r - r'). \quad (19)$$

Taking the integral over latter equation, we see that

$$\int_{r'-\varepsilon}^{r'+\varepsilon} (\hat{h}_0 - E) g_{E\kappa}^{LL}(r, r') dr = \int_{r'-\varepsilon}^{r'+\varepsilon} \delta(r - r') dr = 1$$

should be valid for $\varepsilon \rightarrow +0$ and for any r' and, hence, that — by using Eq. (7) and carrying out some algebraic manipulations — the derivative

$$\left. \frac{\partial}{\partial r} g_{E\kappa}^{LL}(r, r') \right|_{r=r'-\varepsilon}^{r=r'+\varepsilon} = \alpha \left(\frac{2}{\alpha} + \frac{\alpha Z(r')}{r'} + \alpha E \right) \quad (20)$$

'jumps' at $r = r'$. We can use the right hand side of Eq. (20) together with the derivative of Eq. (8) to determine the normalization constants c_f and c_g with which the coefficients $f_{i,j}$ and $g_{i,j}$ need to be multiplied in order to obtain the normalized radial component $g_{E\kappa}^{LL}(r, r')$.

Having constructed $g_{E\kappa}^{LL}(r, r')$ piecewise as solution to Eq. (7), we may obtain the second component $g_{E\kappa}^{SL}(r, r')$ of this pair simply from Eq. (6),

$$g_{E\kappa}^{SL}(r, r') = \frac{\left(\frac{\partial}{\partial r} + \frac{\kappa}{r} \right) g_{E\kappa}^{LL}(r, r')}{\frac{2}{\alpha} + \frac{\alpha Z(r)}{r} + \alpha E}, \quad (21)$$

where the derivatives of the Kummer and Tricomi functions in expressions (13) and (14) can be calculated by means of standard formulae [17]

$$M'(a, b, z) = \frac{a}{b} M(a + 1, b + 1, z), \quad U'(a, b, z) = -a U(a + 1, b + 1, z).$$

In practise, both functions $M(a, b, z)$ and $U(a, b, z)$ are required only for real arguments a , b , and z but need to be calculated with a rather sophisticated algorithm [18] in order to ensure numerical stability and to provide sufficiently accurate results. A similar numerical procedure has to be carry out also for the second pair ($g_{E\kappa}^{SS}$, $g_{E\kappa}^{LS}$) of radial components. This gives rise of course to another set of coefficients $\{\tilde{f}_{i,j}, \tilde{g}_{i,j}\}$ and, finally, to the full radial Green's function from Eq. (4). The $4i_{\max}$ coefficients for the (piecewise) regular and irregular solutions in ansatz (11–12) and (8) certainly provide — together with a few numerical procedures — the most *compact* representation of the radial central-field Green's functions. For the further computation of matrix elements and atomic properties, however, these radial components are usually represented (and stored) at some (2-dimensional) grid in r and r' as we will discuss below.

2.3 Tests on the accuracy of the radial Green's functions

To make further use of the Green's functions in applications, it is necessary to have a simple test on their *numerical* accuracy. For the radial-spherical representation of these functions as defined in Eq. (3), such a test is easily constructed since the Green's function contains the information about the complete spectrum of the Hamiltonian (1) and, hence, about any of its eigenstates $\psi_n(\mathbf{r})$. Making use of the well-known expansion of the Green's function

$$G_E(\mathbf{r}, \mathbf{r}') = \sum_n \frac{\psi_n(\mathbf{r}) \psi_n^\dagger(\mathbf{r}')}{E_n - E}$$

in terms of the eigenstates of the Hamiltonian, the relation

$$\psi_n(\mathbf{r}') = (E_n - E) \int d\mathbf{r} \psi_n^\dagger(\mathbf{r}) G_E(\mathbf{r}, \mathbf{r}') \quad (22)$$

can be easily derived from the orthogonality of the eigenfunctions and holds for all energies $E \neq E_n$. With the representation (3) in mind, the relation (22) can be written also in terms of the radial wave and Green's functions

$$\begin{pmatrix} \tilde{P}_{n\kappa}(r') \\ \tilde{Q}_{n\kappa}(r') \end{pmatrix} = (E_{n\kappa} - E) \int_0^\infty dr (P_{n\kappa}(r), Q_{n\kappa}(r)) \begin{pmatrix} g_{E\kappa}^{LL}(r, r') & g_{E\kappa}^{LS}(r, r') \\ g_{E\kappa}^{SL}(r, r') & g_{E\kappa}^{SS}(r, r') \end{pmatrix}, \quad (23)$$

where $P_{n\kappa}(r)$ and $Q_{n\kappa}(r)$ are the large and small components of the (Dirac) radial 2-spinors. As indicated by the tilde on the left-hand-side of Eq. (23), therefore, this relation may serve as a test on the accuracy of the Green's functions if, for instance, the radial components from both side of the equation are compared with each other or if some proper *overlap* integral is calculated.

To test on the precision of the Green's functions in XGREENS, we generate the radial bound-state wave function $P_{n\kappa}(r)$ and $Q_{n\kappa}(r)$ as solution of the radial Dirac equation

$$\left[-\frac{\alpha Z(r)}{r} - \alpha E \right] P_{n\kappa}(r) + \left[\frac{\kappa}{r} - \frac{\partial}{\partial r} \right] Q_{n\kappa}(r) = 0 \quad (24)$$

$$\left[\frac{\partial}{\partial r} + \frac{\kappa}{r} \right] P_{n\kappa}(r) + \left[-\frac{2}{\alpha} - \frac{\alpha Z(r)}{r} - \alpha E \right] Q_{n\kappa}(r) = 0 \quad (25)$$

with the same potential $-\frac{Z(r)}{r}$ as applied before and by making use of the program by Salvat *et al* [10]. This solver has been embedded in our code and is utilized in order to calculate the relativistic components. With these radial functions, we then compute the two integrals in (23) for obtaining $\tilde{P}_{n\kappa}(r)$ and $\tilde{Q}_{n\kappa}(r)$, respectively, as a function of r . As default in XGREENS, we use the *overlap* integral

$$\int (\tilde{P}_{n\kappa}(r) P_{n\kappa}(r) + \tilde{Q}_{n\kappa}(r) Q_{n\kappa}(r)) dr \quad (26)$$

for the two lowest principal quantum numbers n of the (given) symmetry κ , together with the corresponding *normalization* integral

$$\int (\tilde{P}_{n\kappa}(r) \tilde{P}_{n\kappa}(r) + \tilde{Q}_{n\kappa}(r) \tilde{Q}_{n\kappa}(r)) dr, \quad (27)$$

as a *numerical measure* on the accuracy of the generated Green's functions. These integrals are displayed explicitly by the program (on demand). For a standard (logarithmic) grid with about 300 nodes, the overlap integral (26) is typically within the range $10^{-2} \dots 10^{-3}$. For such a grid, the accuracy is limited in the computations by the linear interpolation of the wave and Green's functions. The accuracy can be increased however for a larger number i_{\max} of grid points as shown in section 4.

3 Program structure

3.1 The RATIP package

Similar as GRASP92 [9] was designed for generating the wave functions within the multi-configuration Dirac-Fock (MCDF) model, the RATIP package [19, 20, 21] is organized as a

suite of program components to calculate a variety of (relativistic) atomic transition and ionization properties. Among other features, the components of RATIP support for instance investigations on the autoionization of atoms and ions, the interaction with the radiation field, the parametrization of angular distributions in the emission of electrons and photons, or the analysis of interference effects between radiative and non-radiative processes. In quite different case studies, RATIP has helped analyze and interpret a large number of spectra and experiments. In order to provide efficient tools for atomic computations, it also incorporates a number of further components (beside of the main program components for calculating certain physical properties) which facilitate the transformation of wave functions between different coupling schemes or the generation of continuum orbitals and angular coefficients. With the development of the XGREENS program, we now provide an additional component to generate the relativistic central-field Green's functions within the RATIP environment. This is rather independent of their later 'use' where different properties such as the two-photon ionization and decay or various polarizabilities of atoms and ions might be calculated with the help of these functions. Owing to the large number of possible applications, however, a support of certain properties will largely depends on the requests by the users and on our further experience with the code.

Not much more need to be said about RATIP's overall structure. A detailed account on its present capabilities has been given previously [22]. With regard to the further development of RATIP, we just note that our main concern now pertains to a long life-cycle of the code and to an object-oriented design within the framework of Fortran 90/95. With the present set-up of the XGREENS component, we continue our effort for providing an atomic code which is prepared for future applications in dealing with open-shell atoms and ions.

3.2 Data structures and program execution

Certainly, the major purpose of XGREENS is the computation of (one-electron) radial Green's functions for some — specified or externally given — central-field potential, which can later be utilized for calculating radial matrix elements of the type

$$U_{\beta\kappa\alpha}^{T_\beta T T_\alpha}(k, \Lambda; E; \tilde{k}, \tilde{\Lambda}) = \int \int_0^\infty g_\beta^{T_\beta}(r) j_\Lambda(kr) g_{E\kappa}^{T\tilde{T}}(r, r') j_{\tilde{\Lambda}}(\tilde{k}r') g_\alpha^{T_\alpha}(r') dr dr', \quad (28)$$

where $j_\Lambda(kr)$ denotes a spherical Bessel function, $g_{E\kappa}^{T\tilde{T}}(r, r')$ one of the components of the radial Green's function in (4), and where α and β refer to the radial wave functions of some bound or free-electron state, respectively. Matrix elements of this type play a key role, for instance, for studying two-photon ionization (bound-free) or decay (bound-bound) processes. Since the (four) components of the radial Green's functions depend on two radial coordinates, r and r' , a rather large amount of data need usually to be calculated by means of XGREENS. These data are finally stored in an external (.rgf) radial Green's function file as will be discussed in the next subsection.

To generate and utilize the Green's functions, two derived data types `TGreens_single_rgf` and `TGreens_rgf` have been introduced as shown in Figure 1. Using these data types, a single Green's function is kept internally in terms of its expansion coefficients from Eqs. (11) and (12) for the *large-large* and a similar set of coefficients for the *small-small* component on the given grid. Apart from the particular representation of the grid, these data structures contain

```

type :: TGreens_single_rgf
-----
! Data structure type to keep a single Green's function
-----
real(dp)                :: energy
integer                 :: kappa
! Coefficients for the regular and irregular solutions
real(dp), dimension(:, :), allocatable :: fLL1, fLL2, fSS1, fSS2
! Values of the regular and irregular solutions and their derivatives
real(dp), dimension(:, :), allocatable :: mL, wL, mS, wS, &
                                         mSp, wSp, mSp, wSp
end type TGreens_single_rgf
!
type :: TGreens_rgf
-----
! Data structure type to save the Green's functions
-----
type(TGreens_single_rgf), dimension(:, :), allocatable :: gf
integer                 :: interpolation_mode, mtp
real(dp), dimension(:, :), allocatable :: yp, z0, z1
end type TGreens_rgf

```

Figure 1: The derived data structures `TGreens_single_rgf` and `TGreens_rgf` to generate, store, and interpolate a central-field Green's function.

the energy and symmetry of the radial Green's function, the nuclear charge function(s) as well as information about the mode of interpolation of the radial components between the grid points and the maximum tabulation point `mtp`. In `XGREENS`, a variable of `type(TGreens_rgf)` is used in order to store the information about all the requested functions, and a few additional procedures are provided to calculate from these structures the values of the radial components for any set of arguments.

The basic steps in the execution of the program are very similar as for other components of the `RATIP` package. At the beginning, all the necessary input data are read in by an (interactive) dialog. The requested Green's functions are then calculated in turn and tested for their accuracy. The (main) output of the program is a formatted ASCII file which provides an interface for further applications, either within the `RATIP` environment or as worked out by the user.

3.3 Interactive control and output of the program

Like the other components of the `RATIP` package, `XGREENS` is controlled by a dialog at the beginning of the execution. In this dialog, all information need to be specified for obtaining the central-field potential as well as about the number and symmetry of the radial Green's functions to be generated. Owing to various choices for defining the spherical potential, however, slightly different dialogs may occur during the execution. An example is shown in Figure 2, where first a Hartree-plus-statistical-exchange (HX) potential due to Cowan [23, 24] is generated from the ground-state wave functions of atomic gold, and then two radial Green's functions are calculated within this potential.

Apart from the nuclear charge, given in terms of a `GRASP92 .iso` isotope data file, the dialog first prompts for specifying (or confirming) some basic parameters such as the speed of light, the grid parameters as well as for the energy units, in which the further input and output is done by the program. This is followed by a prompt for determining the central-field potential for the radial Green's functions. At present, `XGREENS` supports four models including a pure

Coulomb potential (for the calculation of Coulomb Green's functions) as well two potentials (HFS and HX) to incorporate also the *exchange interaction* in some approximate form. In the Hartree model, in contrast, only the *direct* potential of some atomic level is applied in the later computation of the Green's functions. In all these cases, however, the wave functions of the selected state have to be specified in terms of the corresponding `GRASP92` files for the configuration state functions (CSF), mixing coefficients as well as the radial orbitals. If computed internally, the potential can be written also to disc and used in further applications. Beside of the internal set-up of the potential, in addition, a user-defined potential can be given also explicitly and *read in* by the program.

Although the nuclear charge is specified by means of a `.iso` file (in line with all other components of `RATIP`), the Green's functions are always generated for a *point-like* nucleus in order to 'utilize' their regular behaviour of the radial components at the origin [cf. section 2.2]. For each radial Green's function, then the energy and the one-particle symmetry κ need to be specified. The functions are finally written to the `.rgf` radial Green's function file whose name has also to be given at the end of the dialog. In this file, the radial Green's functions are given at the grid (in r and r') as specified originally. Moreover, to test the accuracy of the Green's functions, a number of overlap and normalization integrals are calculated on request in order to 'compare' a few low-lying orbitals, as obtained from the Green's functions by an integration over r' , with independently generated functions from Salvat's program [10]. In average, the computation of a single Green's function requires about 2 min on a 450 MHz Pentium PC and approximately the same time for the 'test' integrals. In the latter case, the rather large demand on CPU time arises mainly from the $2i_{\max}$ radial integrals in r' -space, which need first to be performed in order to obtain the radial orbital functions from the given Green's function components.

3.4 Distribution and installation

A program of `RATIP`'s size cannot be maintained over a longer period without that certain changes and the adaptation of the code to recent developments (in either the hardware or the operating systems) become necessary from time to time. For the distribution of the code, therefore, we follow our previous style in that the `RATIP` package is provided as whole. The main emphasis with the present extension of the program, however, is placed on the design and implementation of the two (new) modules `rabs_greens.f90` and `rabs_utilities_2.f90` which contain the code for the generation and the test of the radial Green's functions. In addition, the four modules (`rabs_special_functions.f90`, `rabs_error_control.f90`, `rabs_greens_external.f90`, and `rabs_cpc_salvat_1995.f`) became necessary and had to be appended to the code in order to support an accurate computation of the hypergeometric and a few related functions from mathematical physics as well as for providing Salvat's solver [10] for the generation of the radial wave functions ($P(r)$, $Q(r)$) within a given potential.

In the present version, the `RATIP` package now contains the source code for the 8 components `ANCO`, `CESD`, `LSJ`, `GREENS`, `RCFP`, `RELCl`, `REOS` as well as the `UTILITIES` for performing a number of small but frequently occurring tasks. Together with the six additional modules from above, the overall program therefore comprises about 40.000 lines of code, separated into 22 modules (apart from the main program components and three libraries). All these source files are provided in the `Ratip` root directory. As before, there is one *makefile* for each individual

component from which the corresponding executable can be obtained simply by typing the command `make -f make-component`, that is `make -f make-greens` in the present case. For most components of the RATIP package, in addition, we provide a test suite in a subdirectory `test-component` of the root where `component` refers to the names above. For example, the directory `test-greens` contains all the necessary files to run the sample calculations which we will discuss below.

Before, however, the makefiles can be 'utilized', a number of global variables need to be specified for the compilation and linkage of the program. In a LINUX or UNIX environment, this is achieved by modifying (and *sourceing*) the script file `make-environment` which saves the user from adopting each makefile independently. In fact, the script `make-environment` just contains a very few lines for specifying the local compiler, the options for the compiler, as well as the local paths for the libraries. Under WINDOWS, in contrast, not much help need to be given to the user since most compiler nowadays provide the feature to define 'projects'. In this case, it is recommended to *read off* the required modules and source files from the makefile of the program component and to 'declare' them directly to the project as associated with the given component.

In the past year, the XGREENS program has been applied under several LINUX systems using the LAHEY Fortran 95 compiler. The RATIP program as a whole has been found also portable rather easily to other platforms such as IBM RS/6000, SUN OS, or to the PC world. The file `Read.me` file in the `ratip` root directory contains further details for the installation. Overall, however, it is expected that it will not be difficult to compile the program also under other operating systems.

4 Test calculations

To illustrate the use of the XGREENS program, we briefly discuss and display two examples. They refer to the generation of the radial Green's function for a few selected (one-electron) symmetries in atomic gold ($Z = 79$) and demonstrate how the accuracy of these functions can be increased by a proper choice of the radial grid. However, before the radial components can be generated, we need first to specify the potential as shown in Figure 2. For the present examples, we have chosen a HX (Hartree-plus-statistical-exchange) due to the work of Cowan [23, 24], starting from the ground-state wave functions of neutral gold. As usual for GRASP92 and RATIP, these wave functions have to be provided in terms of the `.csl` configuration state list and the `.mix` configuration mixing files as well as the `.out` radial orbital file. All of these input files are provided also in the `test-greens/` subdirectory of the `Ratip` root directory and, thus, can be used for the present tests. In Figure 2 moreover, the potential is saved to the central-field potential file `z79-au-hx.pot` and later re-utilized in Figure 3. The output of the two examples are shown in the TEST RUN OUTPUT below.

Like for the wave functions, the 'quality' of the generated Green's functions becomes only fully apparent, if they are used for calculating *observables* which can be compared to experiment. Although calculation of observables is not the aim of the present work, it is still possible to test the accuracy of the generated Green's functions by re-calculating the radial orbitals (as discussed in section 2.3) and by comparing these orbitals with those as obtained from the integration of the Dirac equation for the given central field. This 'comparison' is done in XGREENS

```
XGREENS: Calculation of relativistic central-field Green's functions
with energies E < 0 (Fortran 95 version);
(C) Copyright by P Koval and S Fritzsche, Kassel (2004).

Enter a file name for the greens.sum file:
z79-au-pot.sum
Enter the name of the isotope data file:
z79.iso
loading isotope data file ...
... load complete;
The physical speed of light in atomic units is 137.0359895000000 ;
revise this value ?
n
The parameters of the radial grid 1 (first grid) are
rnt = 2.177968408335618E-04 ;
h = 6.250000000000000E-02 ;
hp = 0.000000000000000E+00 ;
n = 390 ;
revise these values ?
n
Which units are to be used to enter and to print the energies:
A : Angstrom;
eV : electron volts;
Hartree : Hartree atomic units;
Hz : Hertz;
Kayser : [cm**(-1)];
eV
Determine type of central-field potential to generate:
Load : Load a potential from a .pot file
Coulomb : (pure) Coulomb potential
Hartree : Direct potential for a given ASF
HFS : Hartree-Fock-Slater method
HX : Hartree-plus-statistical-eXchange (Cowan 1967)
HX
Enter the name of the .csl (configuration states list) file:
au.csl
Loading configuration symmetry list file ...
There are 22 relativistic subshells;
there are 3 relativistic CSFs;
... load complete.
Enter the name of the GRASP92 mixing coefficient file:
z79-au.mix
Loading mixing coefficients file ...
... load complete;
Enter the name of the rwf data file:
z79-au.rwf
... load complete;
Summary of all ASF to facilitate the selection of proper bound-state levels
-----
i Level J^P Energy (a.u.) Energy (eV)
-----
1 1 1/2 + -1.90397E+04 -5.18096E+05

Enter ASF level number for which the potential should be calculated:
1
Enter the subshell (e.g. 1s, 2p-, ...) which is specific to Cowan's HX method:
1s
Write the generated potential to disc ?
y
Enter the name of .pot central-field potential file:
z79-au-hx.pot
Radial Green's functions will be calculated within the range 0 <= r, r' <= 4.797 a.u.
with the boundaries of the nuclear charge function Z(0) = 79.00 and Z(r_max) = 1.951
In the given potential the one-electron energies (in eV) are:
1s: -8.131E+04
2s: -1.453E+04 2p-: -1.402E+04 2p: -1.214E+04
3s: -3.479E+03 3p-: -3.232E+03 3p: -2.814E+03 3d-: -2.382E+03 3d: -2.289E+03

Enter in turn the energies E (in eV) and symmetries of the radial Green's functions to be generated;
Enter another energy and symmetry (<cr> if done):
-10000 s
Enter another energy and symmetry (<cr> if done):
-15000 d-
Enter another energy and symmetry (<cr> if done):

Check the accuracy of the Green's functions after generation ?
y
Enter the name of .rgf file to save the Green's function:
z79-au-pot.rgf
:
:
```

Figure 2: Interactive dialog for calculating the effective potential and for generating the radial Green's functions.

```

.
.
The parameters of the radial grid 1 (first grid) are
rnt = 2.177968408335618E-04 ;
h = 6.250000000000000E-02 ;
hp = 0.000000000000000E+00 ;
n = 390 ;
revise these values ?
y
Enter rnt:
2.177968408335618E-04
Enter h:
3.125E-2
enter hp:
0
enter n:
780
Which units are to be used to enter and to print the energies:
A : Angstrom;
eV : electron volts;
Hartree : Hartree atomic units;
Hz : Hertz;
Kayser : [cm**(-1)];
eV
Determine type of central-field potential to generate:
Load : Load a potential from a .pot file
Coulomb : (pure) Coulomb potential
Hartree : Direct potential for a given ASF
HFS : Hartree-Fock-Slater method
HX : Hartree-plus-statistical-eXchange (Cowan 1967)
Load
Enter the name of a .pot file with a central-field potential
z79-au-hx.fld
Radial Green's functions will be calculated within the range 0 <= r, r' <= 5.269 a.u.
with the boundaries of the nuclear charge function Z(0) = 79.00 and Z(r_max) = 1.000
In the given potential the one-electron energies (in eV) are:
1s: -8.131E+04
2s: -1.453E+04 2p-: -1.402E+04 2p: -1.214E+04
3s: -3.479E+03 3p-: -3.232E+03 3p: -2.814E+03 3d-: -2.382E+03 3d: -2.290E+03

Enter in turn the energies E (in eV) and symmetries of the radial Green's functions to be generated;
Enter another energy and symmetry (<cr> if done):
-1000 s
Enter another energy and symmetry (<cr> if done):
-10000 s
Enter another energy and symmetry (<cr> if done):
-15000 p
Enter another energy and symmetry (<cr> if done):
-10000 p-
Enter another energy and symmetry (<cr> if done):
-15000 d-
Enter another energy and symmetry (<cr> if done):
-10000 d
Enter another energy and symmetry (<cr> if done):

Check the accuracy of the Green's functions after generation ?
y
Enter the name of .rgf file to save the Green's function:
z79-au-rgf.rgf
.
.

```

Figure 3: Dialog for calculating the radial Green's functions with an increased number of radial points.

on request by evaluating for the two lowest principal quantum numbers n the (radial) overlap integrals of the re-calculated functions with the solutions by Salvat's program. In addition, the *normalization* integrals are also displayed as seen from the TEST RUN OUTPUT. Except of a few cases, the deviation of these integrals from 1.0 are typically well below 0.1 % on the standard grid with about 300 mesh points in r and r' . For these deviations, there are two source of numerical 'inaccuracy' which arise from the test procedure and are not related to the generation of the radial Green's functions. They are caused by the fact that by using Salvat's solver [10], a third-order spline is used to represent the potential at intermediate points in r in contrast to the linear representation (9) for the generation of the Green's functions. Moreover, the integration of the radial integrals uses the standard GRASP92 procedure and, hence, is not adapted as well to Salvat's solutions.

The accuracy of the Green's functions (and the test integrals) can be improved however if the number of grid is enlarged, i. e. the spacing between the mesh points reduced. In our second example, cf. Figure 3, we therefore adopt a grid with approximately twice the number of mesh points. Note that this requires four times as much storage as the radial components are functions in r and r' . In this test case, moreover, the radial Green's functions are generated for four different symmetries s , $p_{1/2}$, $p_{3/2}$, $d_{3/2}$, and $d_{5/2}$. When the TEST RUN OUTPUT from this example is compared with those from example 1, we see that the accuracy in the overlap integrals is increased by about a factor of 5. For this example, the generation and test took about 30 minutes in total on a 450 MHz Pentium III.

After the termination of XGREENS, the radial Green's functions file (e. g. **z79-au-rgf.rgf** from example 2) contains all the Green's function components which were generated during the execution. Since this is a formatted file, it can easily be read and manipulated by any text editor. This (radial Green's function) file stores the individual components $g_{E\kappa}^{TT'}$ (r, r') of the Green's functions as 2-dimensional arrays within a simple file structure. An (internal) file signature # DCFGF in the first line is followed by the mode of interpolation and the number of Green's functions which are provided by the file. Then, each Green's function is specified (in turn), starting with the energy and symmetry of the function and followed by a table of six rows where the first two rows refer to the coordinates r and r' (in atomic units) and the other rows to the four component functions $g_{E\kappa}^{LL}(r, r')$, $g_{E\kappa}^{LS}(r, r')$, $g_{E\kappa}^{SL}(r, r')$ and $g_{E\kappa}^{SS}(r, r')$ in this particular order. Although this format is convenient for the later use of these functions, it may lead to rather large data files, especially if some larger number of Greens' functions need to be generated. In practise, however, not much problems are expected with this file structure because disc storage became cheap recently and because, for most applications, we expect the Green's functions to be generated *on demand* by making use of the corresponding modules instead of keeping them in external files. Typically, the radial wave and Green's functions occur as part of matrix elements and, thus, first require an additional integration (over r and/or r') before any *observable* quantity is obtained.

The format of the radial Green's function (**.rgf**) file can be used easily in order to plot the various radial components. In Figure 4, therefore, we display the nuclear charge function $Z(r)$ and the two radial Green's function components $g_{E_s}^{LL}(r_0, r)$ and $g_{E_s}^{SL}(r_0, r)$ as function of (second) argument r and taken for $r_0 = 0.204076$ a. u. The radial Green's functions are calculated in the ground-state potential of atomic gold, as applied in example 2, for the energy $E = 1000$ eV. As seen from Figure 4, the *large-large* component $g_{E_s}^{LL}$ is continuous at $r = r'$ while the *small-large* component $g_{E_s}^{SL}$ jumps owing to Eqs. (20) and (21) at this position

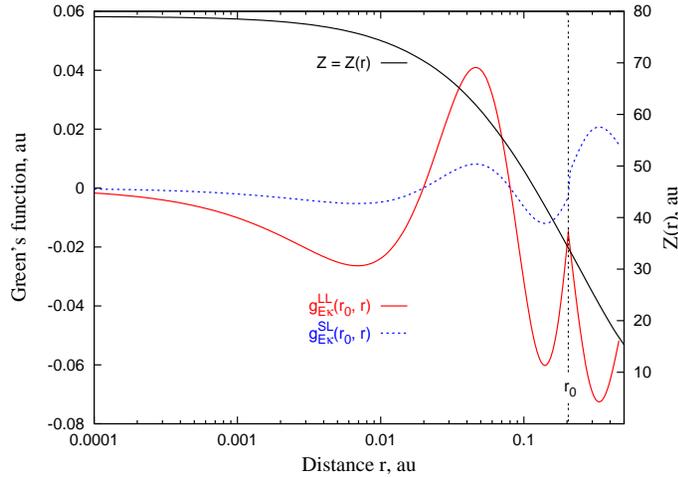


Figure 4: Nuclear charge $Z = Z(r)$ and the radial Green's function components $g_{E\kappa}^{LL}(r_0, r)$ and $g_{E\kappa}^{SL}(r_0, r)$ as function of r and for $r_0 = 0.204076$ a.u. The radial Green's functions with s -symmetry ($\kappa = -1$) are calculated in the ground-state potential of atomic gold for the energy $E = 1000$ eV.

in space. Both components, moreover, behave 'regularly' at the origin as was constructed explicitly by Eq. (8).

5 Outlook. Applications of central-field Green's functions

Apart from fundamental interest in having the central-field Green's functions available for 'relativistic' electrons, these functions are also useful for the perturbative treatment of atoms and ions. As discussed in subsection 2.3, namely, the Green's function provide a simple access to the complete spectrum of a quantum system and, hence, can be utilized for carrying out the summation over all the (one-particle) states of the spectrum as required in second- and higher-order perturbation theory. However, since we only provide the *one-electron* Green's functions, they can be applied for just those processes where the 'perturbations' are described in terms of one-particle operators. Perhaps, the most-studied perturbation of this type is the interaction of atoms and ions with the radiation field, which — within a sufficiently strong field — may lead not only to atomic photoionization but (in second order) also to the two-photon ionization and decay of atoms and ions and to several other processes. During the last two years, we utilized the central-field Green's functions mainly for exploring the two-photon ionization for the helium-like ions and for the inner-shell electrons from atomic neon and argon.

Apart from the one-particle Green's functions (as discussed in this work), there are a number of further processes such as the double Auger decay, for which the *two-particle* Green's functions $G_E(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}'_1, \mathbf{r}'_2)$ are required in order to calculate the cross sections, decay rates and/or angular distributions. These two-particle functions are solutions to a *defining equation* similar to Eq. (2) but where the (one-particle) Dirac Hamiltonian \hat{H}_D is replaced by the two-

particle operator $\hat{H}_{D,1} + \hat{H}_{D,2} + \hat{V}_{12}$, including the electron-electron interaction \hat{V}_{12} explicitly. Even by making use of a proper *radial-angular* decomposition of such Green's functions, their radial part $g_{\kappa_1, \kappa_2}^k(r_1, r_2; r'_1, r'_2)$ would depend then on four radial variables and an overall rank k , similar as known from the tensorial decomposition of the electron-electron interaction [25]. Therefore, an internal representation and generation of these (radial) functions appear rather infeasible in practise. An alternative to these two-particle Green's function is given by the (so-called) *modified pair functions* $\Phi_{E,\alpha}(\mathbf{r}_1, \mathbf{r}_2)$ which satisfy the equation

$$\left\{ \hat{H}_{D,1} + \hat{H}_{D,2} + \hat{V}_{12} - E \right\} \Phi_{E,\alpha}(\mathbf{r}_1, \mathbf{r}_2) = \hat{W} |\Psi_\alpha(PJM)\rangle,$$

where \hat{W} is a one- or two-particle operator which depends on the physical task to be solved and $|\Psi_\alpha(PJM)\rangle$ is one of the (two-electron) solutions of the corresponding homogeneous equation. These modified pair functions have the advantage that they only depend on two radial variables similar as the one-particle Green's functions. On the other hand, of course, these functions now depend on some (initial) two-particle state $|\Psi_\alpha(PJM)\rangle$ as well as on the particular choice of the interaction operator \hat{W} and, hence, are less general when compared with the Green's function from above. We currently investigate the possibilities for generating also such modified pair functions within the framework of RATIP and for their (later) use in the description of the double Auger decay. But already the one-particle Green's functions from this work enables one to explore a number of atomic properties which have not been studied before for complex atoms or, at least, not within a relativistic framework.

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TEST RUN OUTPUT

```
*****
** Example 1 **
*****

Generation of radial Green's functions

-----
i      E (      eV)      j      overall progress
-----
1      -1.000000E+04      s      50%
2      -1.500000E+04      d-     100%

Tests on the accuracy of the Green's functions by means of overlap and normalization integrals:

-----
i      E (      eV)      nj      <nj (Greens) | nj (Salvat 95)>      Normalization
|nj (Greens)||
-----
1      -1.000000E+04      1s      1.000020E+00      1.000057E+00
1      -1.000000E+04      2s      1.001925E+00      1.003888E+00
2      -1.500000E+04      3d-     9.997536E-01      9.995404E-01
2      -1.500000E+04      4d-     1.005937E+00      1.012284E+00
-----

Write the Green's functions to the .rgf file;
2 radial Green's functions with 5065446 bytes ...

XGREENS complete ...
```

```
*****
** Example 2 **
*****

Generation of radial Green's functions

-----
i      E (      eV)      j      overall progress
-----
1      -1.000000E+03      s      16%
2      -1.000000E+04      s      33%
3      -1.500000E+04      p      50%
4      -1.000000E+04      p-     66%
5      -1.500000E+04      d-     83%
6      -1.000000E+04      d      100%

Tests on the accuracy of the Green's functions by means of overlap and normalization integrals:

-----
i      E (      eV)      nj      <nj (Greens) | nj (Salvat 95)>      Normalization
|nj (Greens)||
-----
1      -1.000000E+03      1s      1.000267E+00      1.000540E+00
1      -1.000000E+03      2s      1.000318E+00      1.000641E+00
2      -1.000000E+04      1s      1.000003E+00      1.000010E+00
2      -1.000000E+04      2s      1.000138E+00      1.000278E+00
3      -1.500000E+04      2p      9.993563E-01      9.987343E-01
3      -1.500000E+04      3p      9.999064E-01      9.998404E-01
4      -1.000000E+04      2p-     1.000384E+00      1.000770E+00
4      -1.000000E+04      3p-     1.000216E+00      1.000435E+00
5      -1.500000E+04      3d-     1.000046E+00      1.000107E+00
5      -1.500000E+04      4d-     1.001539E+00      1.003181E+00
6      -1.000000E+04      3d      1.000084E+00      1.000173E+00
6      -1.000000E+04      4d      1.001030E+00      1.002106E+00
-----

Write the Green's functions to the .rgf file;
6 radial Green's functions with 59754187 bytes ...

XGREENS complete ...
```