

Computer Programs in Physics

GRASPC – GRASP package adapted for the generation of continuum orbitals wave functions

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ABSTRACT

The GRASP package (<https://github.com/compas/grasp>) is a widely used tool for performing fully relativistic bound electron structure calculations of atoms. Its latest official release is GRASP2018, but it has been continuously developed since then.

The presented code, GRASPC, is the adaptation of that package allowing for calculations of the continuum orbital of electrons elastically scattered from atoms and ions. The calculated continuum orbital can be normalized using the per-energy normalization procedure. Then, the phase shifts are calculated by comparing the computed wave function with the free electron wave function in the asymptotic region. Scattering lengths are estimated not only for widely used very low energy scattering but also using an unusual approach with a “zero energy” wave function.

The main idea behind GRASPC is to use as many computational apparatus as they are implemented in GRASP (e.g., building the atomic and configuration state functions, calculating the potentials, angular coefficients and integrals, constructing the Dirac-Coulomb Hamiltonian, performing self-consistent calculations) by adapting them to calculate the wave function of the scattered electron. This adaptation is entirely transparent for usual calculations in GRASP (bound states and their properties). The default flow changes only when calculations involving continuum orbital are requested and different outputs are produced. This approach, combined with the retention of the typical interactive user interface, allows GRASP users to adapt rapidly to the new type of calculation.

PROGRAM SUMMARY

Program Title: GRASPC

CPC Library link to program files: <https://doi.org/10.17632/hg5yp8zfc5.1>

Developer's repository link: <https://github.com/sylaspg/grasp-continuum>

Licensing provisions: MIT

Programming language: Fortran 95

Nature of problem: In electron scattering from atoms and ions, continuum orbitals refer to the quantum states of an electron that is not bound to an atom or ion but instead exists in the continuum of energy levels above the ionization threshold. These orbitals describe the wave functions of free or quasi-free electrons that are involved in scattering processes. Here, we focus only on elastic scattering, occurring mostly at low energies. That means that the electron's kinetic energy remains unchanged.

Solution method: The relativistic multiconfiguration Dirac-Hartree-Fock method (RMCDHF) is used [1]. The scattering problem is constructed as $N + 1$ electron system, where N electrons are bound (with discrete, negative energy levels), and one electron is from the continuum spectrum, with given (positive) energy and the quantum number κ [2]. Then, the radial parts of the large and small components of the continuum orbitals are obtained by solving the Dirac-Hartree-Fock equations using the outward integration method implemented in GRASP2018 [3]. The resulting continuum wave function may be optimized using *per energy* normalization, described in [4].

Additional comments including restrictions and unusual features: The current version of the code is limited to elastic processes. In addition to generating

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the (relativistic) continuum orbital wave functions, the program can calculate phase shifts and scattering lengths. The scattering lengths can be calculated using the well-known formula involving the phase shift, and the “zero energy” approach [5], which gives more accurate results.

The polarization potential is modeled in a three-term form, constructed from the static dipole, quadrupole, and octupole polarizabilities. The dipole term can be automatically included using the latest (experimental and theoretical) data available for the static polarizability of a dipole [6]. The parameters of the quadrupole and octupole terms must be entered manually; otherwise, they will not be included. It should be kept in mind that these terms are representing only static polarizabilities of the target. Alternatively, the polarization potential on a radial grid can be supplied in numerical form in a file.

This code is just an extension of the GRASP package with the new features. All rights to the original GRASP package remain with its authors.

References

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1. Introduction

The scattering of electrons by atoms and ions plays a fundamental role in understanding atomic and molecular structures (see [1–3] and references therein). This process occurs when an electron interacts with the electrostatic potential of an atom or ion, resulting in a change in its trajectory. The nature of this interaction depends on both the incident electron’s energy and the target characteristics. Scattering is predominantly elastic at low energies, meaning the electron’s kinetic energy remains unchanged. However, inelastic scattering can occur at higher energies, leading to energy loss through processes such as excitation or ionization of the target.

In this study, we focus exclusively on elastic scattering, essential for applications in electron microscopy, spectroscopy, and plasma diagnostics. Additionally, precise scattering data contribute to refining theoretical atomic structure and electron interaction models, with significant implications for materials science and quantum mechanics. By analyzing scattering phenomena, researchers gain insights into electron density distributions, potential energy surfaces, and the electronic states of atoms and ions.

Unlike bound atomic or molecular orbitals, relativistic continuum orbitals correspond to positive-energy solutions of the Dirac equation, representing electrons that remain free after scattering. Understanding these orbitals is crucial for determining the phase shifts of partial waves, which, in turn, allow for the calculation of key scattering parameters such as total, differential, momentum transfer, and spin polarization cross sections, as well as the scattering length. The latter parameter is particularly significant in describing electron interactions in cold and ultra-cold collisions, where quantum effects dominate.

There are a few software packages which are intended to calculate the relativistic continuum wave functions. Perger et al. [4] wrote the continuum wave function solver (CONTWVG) for GRASP, but it is limited to the very old GRASP version [5]. This code has been rewritten further to form a standalone package CONTWVSA [6] which has a user interface that is quite difficult to use, however. The ELSEPA [7] is a widely used code, but it is limited to atoms only and electron energies above several dozen eV. The RATIP package [8], on the other hand, has the module COWF (Continuum Orbital Wave Function) which (after some modifications and adaptations) has been successfully used in several cases ([9–12]), but as the Perger’s code [4] is bound to the old GRASP version [5]. Its user interface is quite modern, but calculations run rather slowly. The JAC code [13] may be considered as the successor of RATIP – it is written in a modern programming language and contains a lot of modules for calculations of several atomic processes, but in the current version, it does not implement the exchange potential, which is crucial in low-energy calculations. Lastly, the DARC (Dirac Atomic R-matrix Codes) code [14] has been published to study of continuum processes for a general atomic system. But, even according to its manual [15], it is outdated (bound to the old GRASP version), old-fashioned and inefficient (this has been resolved by introducing the parallel version of the code [16]).

The proposed GRASPC package is based on the continually developed GRASP in its latest version. It is extremely fast, with typical running times not exceeding several seconds, and can handle very low energies, around 0.00001 eV or lower.

Furthermore, since it is a fork of GRASP, any updates or changes made to GRASP will be easily integrated into GRASPC. Additionally, GRASP’s latest version features an easy-to-use, interactive interface, allowing any GRASP user to effortlessly adapt to new types of calculations.

2. Physical background

Here, we focus on the generation of the continuum states only, and their properties. For general information of the theory and calculations of the bound states we refer to [17].

2.1. Generation of the continuum orbital wave function

Within the frames of the relativistic multiconfiguration Dirac-Hartree-Fock method (RMCDFH) [17], the scattering system is constructed as $N + 1$ electron system [10], where N electrons are bound (with discrete, negative energy levels), and one electron is from the continuum spectrum, with given (positive) energy ϵ and quantum number κ .

To obtain the large $P_{\kappa\epsilon}(r)$ and small $Q_{\kappa\epsilon}(r)$ components of the continuum orbitals, the Dirac-Hartree-Fock equations [18]

$$\left(\frac{d}{dr} + \frac{\kappa}{r}\right)P_{\kappa\epsilon} = \left(\frac{2}{\alpha} + \alpha(\epsilon - V - V_{pol})\right)Q_{\kappa\epsilon} - X^{(Q)} \quad (1)$$

$$\left(\frac{d}{dr} - \frac{\kappa}{r}\right)Q_{\kappa\epsilon} = -\alpha(\epsilon - V - V_{pol})P_{\kappa\epsilon} + X^{(P)}, \quad (2)$$

are solved using the *outward* integration method implemented in GRASP [19]. In the above equations, α is the fine structure constant, ϵ is the energy of the scattered particle, $V = V(r)$ is the Coulomb potential, $V_{pol} = V_{pol}(r)$ is a polarization potential, and $X^{(P)}$ and $X^{(Q)}$ are the exchange terms.

Then the continuum Dirac spinor is defined as [18]

$$u_{\kappa m}(\mathbf{r}) = \frac{1}{r} \begin{pmatrix} P_{\kappa\epsilon}(r)\chi_{\kappa m}(\hat{\mathbf{r}}) \\ iQ_{\kappa\epsilon}(r)\chi_{-\kappa m}(\hat{\mathbf{r}}) \end{pmatrix}. \quad (3)$$

The spin-angular function is given by

$$\chi_{\kappa m}(\hat{\mathbf{r}}) = \sum_{\sigma=\pm 1/2} \langle jm|l, \frac{1}{2}, m-\sigma, \sigma \rangle Y_l^{m-\sigma}(\hat{\mathbf{r}}) \chi_{1/2}^{\sigma}, \quad (4)$$

where $\langle jm|l, \frac{1}{2}, m-\sigma, \sigma \rangle$ is the Clebsch-Gordan coefficient, $Y_l^{m-\sigma}(\hat{\mathbf{r}})$ is the spherical harmonic, $\chi_{1/2}^{\sigma}$ is the spin eigenfunction, j is the total angular momentum, l is the orbital quantum number, and m is the magnetic quantum number. Quantum number κ satisfies the relation: $\kappa = \pm(j + 1/2)$ for $l = j \pm 1/2$.

If the calculated wave function is to be coupled with some other function (e.g., the bound state), it should be normalized first. The currently implemented *per energy* continuum wave function normalization is described in [20]. Normalization is usually not required for calculations of phase shifts and scattering lengths.

2.2. Polarization potential

The polarization potential in the scattering of electrons from atoms/ions arises due to the induced interaction between the incident electron and the target. This potential accounts for the fact that the incident electron distorts the electron cloud of the target atom, creating an induced dipole moment that affects the electron's trajectory.

The polarization potential consists of dipole, quadrupole and octupole polarization terms. It is currently implemented in the following form:

$$V_{pol}(r) = -\frac{1}{2} \frac{\alpha_d r^2}{(r^3 + \langle r_0^3 \rangle)^2} - \frac{1}{2} \frac{\alpha_q r^4}{(r^5 + \langle r_0^5 \rangle)^2} - \frac{1}{2} \frac{\alpha_o r^6}{(r^7 + \langle r_0^7 \rangle)^2} \quad (5)$$

where α_d , α_q and α_o represent the static dipole, quadrupole and octupole polarizability, respectively; $\langle r_0^3 \rangle$, $\langle r_0^5 \rangle$ and $\langle r_0^7 \rangle$ are the cut-off parameters.

The best source we know of that provides a comprehensive list of static dipole polarizabilities for atoms is [21] (except for the Livermorium atom, atomic number 116). Unfortunately, there is no similar listing for static quadrupole and octupole polarizabilities.

For atoms, cut-offs $\langle r_0^3 \rangle$, $\langle r_0^5 \rangle$ and $\langle r_0^7 \rangle$ can be taken from bound states calculations, assuming that $\langle r_0 \rangle$ is the radius of the outermost orbital of the target atom.

Polarization potential can also be provided in numerical form in a file, as the set of pairs r $V_{pol}(r)$ (in Bohr radii a_0 , and hartree units, respectively).

2.3. Phase shifts

Relativistic phase shift δ_l is obtained by comparing the numerical solution with the asymptotic one at large r [10], determined to the nearest 2π :

$$P_{\kappa}(r)/r = j_l(kr) \cos(\delta_l) - n_l(kr) \sin(\delta_l), \quad (6)$$

where $j_l(kr)$ and $n_l(kr)$ are the spherical Bessel functions of the first and the second kind, respectively, and $k = \sqrt{2\epsilon + \alpha^2 \epsilon^2}$ is the wavenumber. Orbital angular momentum quantum number l is related to κ such that $\kappa = l$ or $\kappa = -l - 1$, whereby $\kappa \neq 0$. Therefore, for the l -th partial wave (except the $l = 0$ case), we obtain two phase shifts, sometimes referred as δ_l^+ and δ_l^- .

To correctly determine the phase shift, the continuum orbital has to be calculated far enough from the origin to ensure that all potentials can be neglected.

2.4. Scattering lengths

Scattering length is one of the most useful parameters for describing low-energy electron-atom collisions. It is defined as the radius of a rigid sphere in the zero-energy total cross-section. The sign of a scattering length represents the type of interaction: positive for repulsion and negative for attraction.

The common method for determining the scattering length a involves analyzing the asymptotic behavior of the wave function:

$$a = -\lim_{k \rightarrow 0} \frac{\tan(\delta_0)}{k}, \quad (7)$$

where δ_0 is the phase shift for $l = 0$ (*s*-wave, $\kappa = -1$), calculated for (energy-dependent) wavenumber tending towards zero in the limit.

In addition to the above method (which is subject to the inaccuracy associated with the non-zero energy), the calculation of the scattering length is implemented as the intersection of the asymptote of the zero-energy ($\epsilon = 0$) wave function with the r -axis. It comes from the fact that the solutions to the Dirac equation with zero energy and at the lack of potential are

$$P_{\kappa 0}(r) = \frac{2C}{\alpha(2\kappa + 1)} r^{\kappa+1} + D r^{-\kappa} \quad (8)$$

$$Q_{\kappa 0}(r) = C r^{\kappa}, \quad (9)$$

where C and D are constants obtained from integration. Especially, for *s*-wave we get

$$P_{\kappa 0}(r) = -\frac{2C}{\alpha} + Dr = D(r - a) \quad (10)$$

$$Q_{\kappa 0}(r) = \frac{C}{r}, \quad (11)$$

where $a = 2C/\alpha D$ is the scattering length. The details of that approach are described in [12].

3. Computational procedure

The core concept of GRASPC is to utilize as many computational apparatus from GRASP as possible (e.g., building the atomic state function and configuration state functions, calculating the direct and exchange potentials, angular coefficients and integrals, constructing the Dirac-Coulomb Hamiltonian, performing self-consistent calculations; see [17] for details) and only adapt them for calculating the wave function of the scattered electron. This ensures high calculation accuracy with high performance. This adaptation remains seamless for standard GRASP calculations, such as bound states and their properties.

The main difference, which distinguishes the calculation of continuous states from bound states, lies in how the Dirac-Hartree-Fock equation is integrated. Here, you only need to carry out the *outward* integration (in the r limit from 0 to ∞), instead of typical for bound states *outward* ($r \in [0, JP]$) and *inward* ($r \in [\infty, JP]$) where JP is so-called *joint point* which has to be found.

Moreover, the energy of the continuum electron is fixed rather than determined during the self-consistent field (SCF) procedure, as is the case with bound electrons.

An initial estimate of the radial wave function of the continuum can be obtained in the usual way, using the sieved hydrogen model or the Thomas-Fermi model [17]. This approach usually works well, but in some cases it can cause problems with convergence, since the wave function generated in this way decays to zero. Typically, this should not cause problems with continuum spectrum solutions, but unfortunately, sometimes (quite rarely) it does, most likely because of the way the starting points for the integration of the equations are determined in GRASP. As a solution, a new method has been introduced, which allows to obtain a nonzero value of the radial wave function at some distance from the nucleus. This method involves setting a constant value across the whole r -domain. We have verified on a large number of tests that this way of determining the estimate does not cause convergence problems anymore.

The potential in which the wave function is determined is supplemented by a polarization potential of the form given by Eq. (5), or its values may be read from a file.

The radial grid in GRASP is defined by the following parameters:

- N – number of grid points, default 590,
- RNT – value (in a_0) of the first point on the grid (default is $2^{-6}/Z$, where Z is the atomic number),
- H – step size (in a_0), default is 0.05,
- HP – default value 0 means that exponential grid will be used; the other value forces the linear-logarithmic grid and represents the step (in a_0) at its end.

In the case of exponential grid ($HP = 0$), the grid points are defined as $r_j = RNT[e^{(j-1)H} - 1]$, $j = 1, \dots, N$. In the case of linear-logarithmic grid ($HP \neq 0$), grid points are defined by the following relation: $\ln(r_j/RNT + 1) + (H/HP)r_j = (j-1)H$, $j = 1, \dots, N$.

Since the continuum radial wave function of the electron is characterized by non-decaying oscillations far from the atom, the computational grid used must be sufficiently long and dense. Thus, the number of points on the grid N is increased from 590 (the default value in GRASP) to 5000, which translates into a_0 units of hundreds or even thousands. In addition, the user is asked to use a linear-logarithmic grid, which, unlike the usual exponential one, retains a constant step HP at its end.

The resulting radial wave function may be *per energy* normalized [20]. Usually, that procedure is not necessary to determine phase shifts and/or scattering lengths. However, when the wave function is used in calculations involving electric dipole moments (EDMs), normalization should always be performed [11].

As the final step, additional properties not applicable in bound-type calculations are determined, phase shift (6) and scattering length (7). In a special case, when the energy of the scattered electron is set to zero, the scattering length is determined in a special way, as described in Section 2.4 and in [12]. This, in general, should give a more accurate result.

4. User guide

The GRASPC installation process is identical to GRASP, except for the Git repository URL address, which is <https://github.com/sylaspg/grasp-continuum> for GRASPC. That repository should be cloned to a local disk; then the executables are to be built using *CMake* (recommended) or *make*. After successful compilation and installation, all the executables will be located in the `bin` folder. No new executables, other than those typical of GRASP, are created.

The whole process is described in detail in the provided `README` text file, as well as in the well-formatted in Markdown markup language and more extensive `README.md` file.

The default GRASP workflow is altered only when computations involving continuum orbitals are requested, resulting in different inputs and outputs. By maintaining the familiar interactive user interface, this approach enables GRASP users to adjust to the new type of calculation in GRASPC quickly. We have included a typical procedure below.

The assumption is made that all created executables are located in the directory which is added to the `PATH` environmental variable.

4.1. Bound states

The very first step is to optimize bound states of the selected target (atom/ion) in a usual way (`rnucleus => rcsfgenerate => rwnestimate => rangular => rmcdf => rsave` in the simplest case), or take nuclear data (`isodata`) and radial wave functions (`rwn.out / .w`) files from previous calculations.

The above calculations may be performed using GRASP or GRASPC, since they work identically for bound states.

4.2. CSF list

By invoking `rcsfgenerate`, create a special `rcsf.inp` file with only one configuration state function (CSF), where *core* is the configuration of the target atom or ion, and *peel* consists of *one* additional *inactive* electron. This electron will be treated as a scattered one; its principal quantum number will be ignored, and its quantum number κ will be determined from the subshell designation and final J value, resulting from coupling with the core.

For example, for argon-electron scattering, we could have:

- Core subshells: 1s 2s 2p- 2p 3s 3p- 3p
- Additional subshell:
 - 4s(1, i), coupled to $J = 1/2$ means s-wave electron of $\kappa = -1$
 - 4p(1, i), coupled to $J = 1/2$ means p-wave electron of $\kappa = 1$
 - 4p(1, i), coupled to $J = 3/2$ means p-wave electron of $\kappa = -2$
 - 4d(1, i), coupled to $J = 3/2$ means d-wave electron of $\kappa = 2$
 - 4d(1, i), coupled to $J = 5/2$ means d-wave electron of $\kappa = -3$, etc.

Please remember to provide the J value as $2J, 2J$ range (e.g. 1,1 for $J = 1/2$), and to provide 0 as the number of excitations.

Example `rcsf.inp` file for electron-argon scattering (s-wave):

```
Core subshells:
 1s  2s  2p- 2p  3s  3p- 3p
Peel subshells:
 4s
CSF(s) :
 4s ( 1)
      1/2
      1/2+
```

4.3. Angular coefficients

Run `rangular` as usual (with *Full interaction* option enabled).

4.4. Initial estimations of the radial wave functions

Run `rwfnestimate` using the previously calculated radial wave functions as initial estimation for the *core* orbitals (option 1 – *GRASP92 File*). To estimate the additional electron designed to be a continuum one, use the new option 5 – *Continuum orbital*. Any other method (options 2 – 4) should also work (try them if you encounter convergence problems during the actual calculations in the next step).

4.5. SCF procedure

Invoke `rmcdhdf`, then

- answer *n* when asked about *Default settings*?
- answer *y* when asked about *Perform continuum wave function calculations*?
- provide continuum electron energy in hartree (should be positive or zero for accurate scattering length calculation)
- decide if polarization potential should be included.
 - 0 – do not include polarization potential
 - 1 – include the dipole term of the model potential with default parameters: α_d taken from [21], and cut-off $\langle r_0^3 \rangle$ taken from bound state calculations as the size of the outermost orbital; here, the quadrupole and octupole terms are omitted
 - 2 – include model potential with all parameters provided manually by the user; in turn: α_d , $\langle r_0^3 \rangle$, α_q , $\langle r_0^5 \rangle$, α_o and $\langle r_0^7 \rangle$
 - 3 – include numerical potential from the text file named `vp01`, containing pairs r $V_{pol}(r)$ on consecutive lines (in a_0 and hartree units, respectively), ordered by increasing r values, separated by one or more spaces:


```
r0  Vpol(r0)
r1  Vpol(r1)
r2  Vpol(r2)
and so on (as an example, see the Test Case 2).
```
- decide (y/n) if the calculated continuum wave function should be normalized
- answer *y* when asked *Change default speed of light or radial grid parameters*?
- answer *y* when asked *Revise default radial grid parameters*?
- enter new *RNT* and *H* values (firstly, the defaults might be kept)
- enter new *HP*; this value is the step at the tail of the grid, use non-zero value to force the linearly-logarithmic grid, which ensures adequate grid density far from the scattering center; 1.0 or less is the good choice for a first try
- enter new *N*; in general, use as a big number as possible to ensure as long grid as possible; 5000 is the default, but even tens of thousands of points might be required in some cases, which would require code modification (*NNNP* value in `parameter_def_M.f90` in the `src/lib/libmod` folder) and recompilation

If calculations do not converge (*Maximal iterations exceeded*), experiment with the other grid parameters, and/or try the other method to estimate the radial wave function for the continuum electron.

4.6. Output

The calculated continuum orbital wave function will be stored in the `rwfn.out` file (together with the bound orbitals), and also in a text-formatted file `continuum.csp`.

If the grid is long enough and electron energy is not zero, calculated phase shift and scattering length are written to the screen and to the `rmcdhf.sum` summary file. The accuracy of the scattering length strongly depends on the electron energy; smaller energy values yield better accuracy, as the calculation is performed in the $k \rightarrow \infty$ limit.

Suppose the electron energy is set to zero. In that case, only the scattering length is calculated in a more accurate approach, as the intersection of the asymptote of the zero-energy wave function with the r -axis. In that case, additional information is given, which may be helpful for error estimation. The first one is the relative error of straight line determination at the tail. The second one is the percentage difference between the scattering length calculated from the last two points on the grid, specifically the penultimate and the one before the penultimate point. In both cases, a lower value means better accuracy.

5. Test cases – elastic scattering of electrons from argon atoms

Easy-to-run test cases have been prepared to demonstrate the GRASPC package's ability to generate the relativistic continuum spinor and calculate corresponding phase shifts and scattering lengths. The target has been chosen as the argon atom in the ground state.

The parameters of the test cases were chosen so that the results could be easily compared with the results from [2], for both phase shifts and scattering lengths.

All the files needed to perform the tests are located in the `grasptest/continuum/argon-electron_scattering` directory. Particular test cases 1, 2 and 3 described in this section are to be run by invoking the Linux `sh` scripts:

```
1_Ar_continuum_electron_s-wave_function,
2_Ar_continuum_electron_d-wave_function, and
3_Ar_electronic_scattering_length.
```

These scripts contain a sequence of calls to the relevant programs, and the input they need. Their use simplifies the calculation process, freeing the user from having to enter the input data each time manually. The scripts are supplemented with comments that can help. They are written in the same manner as the test script for "pure" GRASP.

The auxiliary script `Ar_bound_DF` generates bound orbitals of the argon atom, using GRASP in its usual sequence of calls. There is no need to run it separately; is invoked automatically at the beginning of each test case. For simplicity, radial wave functions for the ground state of argon are calculated in the Dirac-Fock approximation. That approximation is good enough for demonstrating purposes, but in actual calculations, it should be replaced with the correctly correlated bound state wave functions.

During the calculations, several output files are generated. We refer to the GRASP manual [22] for a complete reference of the format and purpose of each file. The set of typical output files is supplemented by the new unformatted text file, `continuum.csp`, containing calculated continuum spinor. Also, the `rmcdhf.sum` file is slightly modified, with additional information about the calculations performed.

Before running the test, it is recommended to delete all of the output files from the previous run. It can be done by executing the `clean` script.

Test case 1

Generation of the continuum orbital wave function and phase shift calculation for electron of $\kappa = -1$ (s -wave, $J = 1/2$), and energy $\epsilon = 0.00124997$ Hartree $= 0.03401334$ eV ($k = 0.05$), using the model polarization potential (dipole term only)

To run the test, execute the `1_Ar_continuum_electron_s-wave_function` script from the `sh` or `Bash` shell. In addition to generating wave functions for bound states, the most important steps in the script are:

- (lines 21–30) Adding one additional orbital with just one electron to the list of configuration state functions (CSF), which will be treated as continuum one in the SCF procedure. Here, it is $4s(1, i)$ for s -wave (principal quantum number will be ignored), and $J = 1/2$.
- (lines 43–50) Setting initial estimates of radial wave functions for the SCF procedure. For bound states, they are taken from the Dirac-Fock approximation, generated by the previously mentioned `Ar_bound_DF` script. For the continuum orbital, initial estimate is generated using the dedicated method described in the text above.
- (lines 57–75) Running SCF procedure for continuum wave function calculation. Here, an electron energy has been provided (line 61) corresponding to $k = 0.05$, the model polarization potential with default parameters is included (line 1), and the grid has been changed to the linear-logarithmic one (lines 66–70).

Generated console output related to the continuum orbital calculations will look like this:

```
(...)
Setting up the polarization potential
<R0^3> is taken from size of the 3p orbital
Include model polarization potential, alpha_d = 11.0830000000, <R0^3> = 7.7641965142
(...)
Continuum orbital wave function calculations have been performed.
Orbital 4s (no. 8) was marked as continuum (kappa = -1, energy = 0.0012499700 hartree)
```

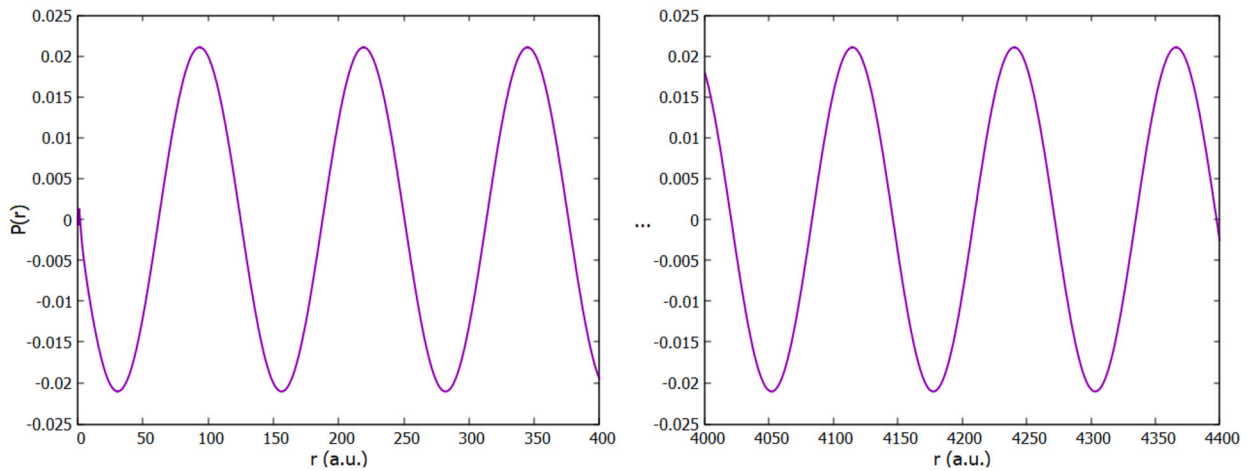



Fig. 1. Calculated continuums-wave function. To the left – close to the origin; to the right – far from the origin.

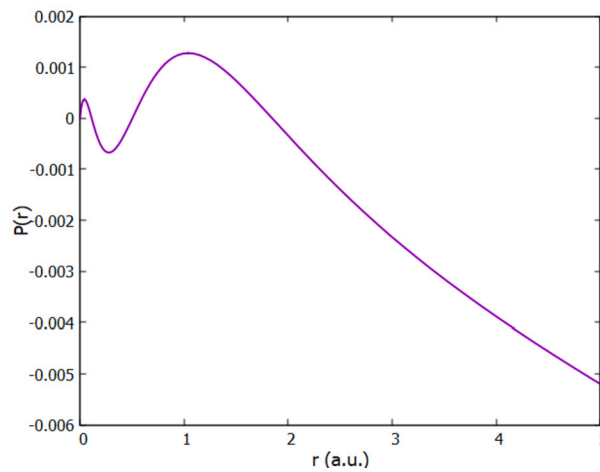


Fig. 2. Calculated continuum s-wave function, very close to the origin.

```

Difference between the analytical and numerical wavelength of the continuum spinor = 0.00132798%
Radial grid: Rmax = 4495.58, Rstep = 1.00
The radial grid is long enough to calculate the phase shift.
Phase shift = -3.1072761138182852 = 3.4316539771507948E-002

Scattering length = -0.68659943463544770
(this is just an estimate, calculated from the phase shift of non-zero energy continuum spinor;
to have a more accurate result, repeat the calculation with zero energy)

The continuum orbital is saved to 'continuum.csp' file.
(...)

```

Resulted continuum spinor is plotted in Figs. 1 and 2. Calculated phase shift, $\delta_0 = 0.03432$ stays in good agreement with result of Cheng et al. [2], 0.03999. It should be noted here, that the phase shift is determined to the nearest 2π , and in many scientific publications is given in the $[-\pi, \pi]$ range. Thus, the calculated value is shifted by 2π if necessary, giving the second, equivalent value in the output (as it was in this case).

Test case 2

Generation of the normalized continuum orbital wave function and phase shift calculation for the electron of $\kappa = 2$ (d-wave, $J = 3/2$), and energy $\epsilon = 0.04499880$ Hartree = 1.22448022 eV ($k = 0.3$), using the polarization potential given in numerical form

To run the test, execute the `2_Ar_continuum_electron_d-wave_function` script. Here, the continuum spinor will be normalized (line 57). Moreover, the additional file `vp01` was prepared, containing numerical values of the polarization potential, taken from [23,24]. It contains pairs of numbers `r` `vp01(r)` (in a_0 and hartree units, respectively):

```

1.00000E-05      -5.40690E-08
1.05127E-05      -5.68411E-08
1.10517E-05      -6.28067E-08

```

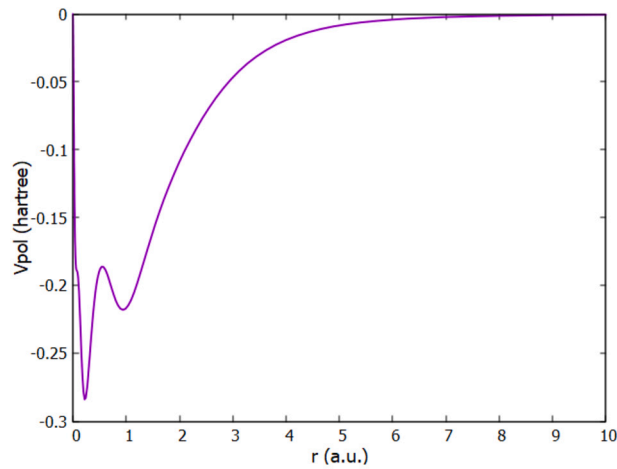


Fig. 3. Polarization potential used in calculations.

```
1.16183E-05      -6.93969E-08
1.22140E-05      -7.66768E-08
(...)
3.42775E+02      -3.90076E-10
3.60350E+02      -3.19367E-10
3.78825E+02      -2.61476E-10
3.98248E+02      -2.14078E-10
```

The polarization potential is plotted in Fig. 3. Output from the script looks like this:

```
(...)
Setting up the polarization potential
Include polarization potential: read from the 'vpol' file.
(...)
Continuum orbital wave function calculations have been performed.
Orbital 4d-(no. 8) was marked as continuum (kappa = 2, energy = 0.0449988000 hartree)
Performing normalization of the continuum wave function.

Difference between the analytical and numerical wavelength of the continuum spinor = 0.00559861%
Radial grid: Rmax = 905.53, Rstep = 0.20
The radial grid is long enough to calculate the phase shift.
Phase shift = 3.2408797325361505E-002

Scattering length = -0.10806716472005916
(this is just an estimate, calculated from the phase shift of non-zero energy continuum spinor;
to have a more accurate result, repeat the calculation with zero energy)

The continuum orbital is saved to 'continuum.csp' file.
(...)
```

Resulted continuum spinor is plotted in Fig. 4. Here, the calculated phase shift, $\delta_2^+ = 0.03241$, stays in almost perfect agreement with the result of Cheng et al. [2], 0.03253.

Test case 3

Scattering length calculations using the zero energy approach, including both dipole and quadrupole terms of model polarization potential

This case demonstrates the GRASPC package's ability to calculate the electronic scattering lengths using the zero-energy approach. Here, apart from choosing *s*-wave (line 18), the crucial thing is to put 0.0 as the energy of the incident electron (line 52 in the `3_Ar_electronic_scattering_length` script). Polarization potential is modeled as dipole and quadrupole terms, while the octupole term was omitted (lines 53–59). The output will look like this:

```
(...)
Setting up the polarization potential
Include model polarization potential, alpha_d = 11.0830000000, <R0^3> = 7.7642000000
Include quadrupole term, alpha_q = 0.1400000000, <R0^5> = 65.7347000000
(...)
```

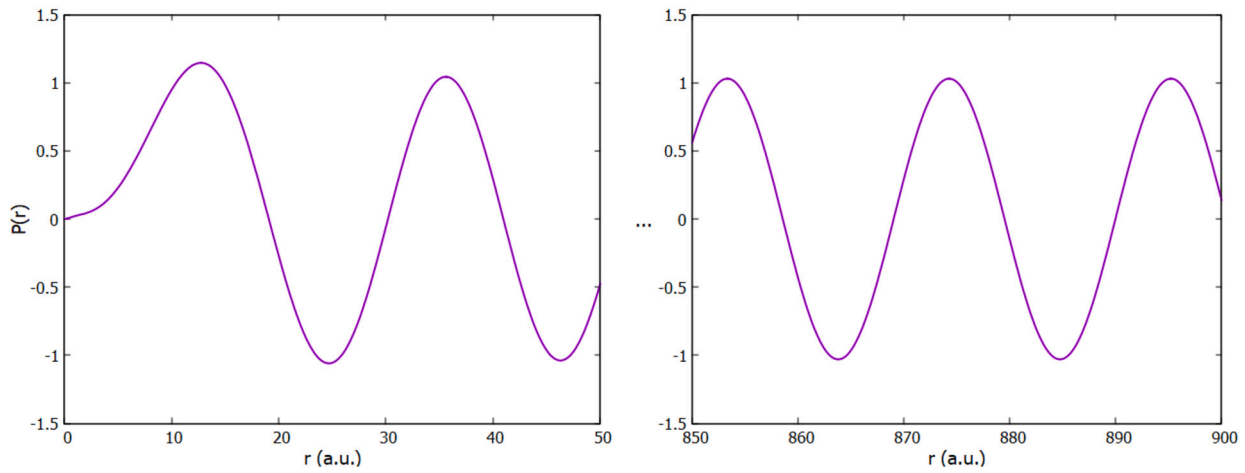



Fig. 4. Calculated continuum d -wave function. To the left – close to the origin; to the right – far from the origin.

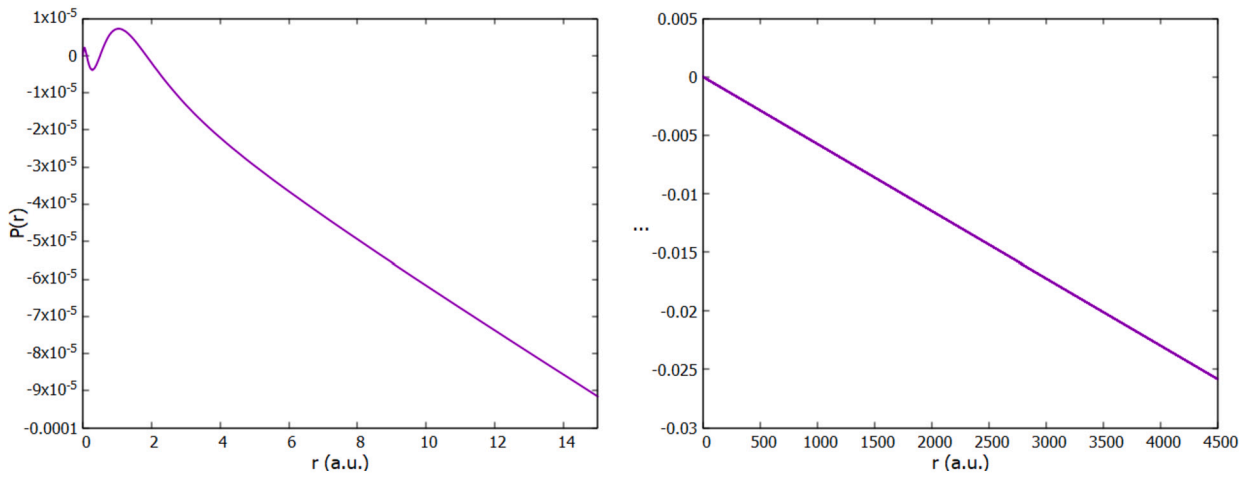


Fig. 5. Calculated continuum s -wave function for zero-energy of the electron. To the left – close to the origin; to the right – far from the origin (straight line, as expected).

Continuum orbital wave function calculations have been performed.
Orbital 4s (no. 8) was marked as continuum ($\kappa = -1$, energy = 0.0000000000 hartree)

Zero energy case, skipping phase shift calculation.

Scattering length = -1.3208745746046964

Information for error estimation:

Radial grid: Rmax = 4495.58, Rstep = 1.00

Relative error of straight line determination at the tail = 0.00000003%

Difference between two consecutive estimates of scattering length = 0.00004181%
(calculated from the last two points on the grid, and the two penultimate points)

The continuum orbital is saved to 'continuum.csp' file.

(...)

Calculated scattering length, $a_0 = -1.320$, although calculated based on bound states coming from Dirac-Fock approximation only, stays in quite good agreement with [2] (-1.39) and [12] (-1.394).

Resulted continuum spinor is plotted in Fig. 5.

6. Conclusions

The GRASP package, used to calculate bound states, has been adapted to calculate wave functions of electrons from the continuum spectrum, along with calculations of phase shifts and scattering lengths. Any existing GRASP user should be able to use it without too much trouble, due to using of the original user interface, expanded only with new features. The test cases presented demonstrate how to use the package and prove the correctness of the results for scattering electrons from argon atoms.

The package is constantly being expanded of the new features, documentation and the test cases. Its latest version can be found on GitHub: <https://github.com/sylaspg/grasp-continuum>

CRedit authorship contribution statement

Paweł Syty: Writing – original draft, Visualization, Software, Resources, Methodology, Investigation. **Michał Piłat:** Writing – review & editing, Validation, Methodology, Investigation. **Józef E. Sienkiewicz:** Writing – review & editing, Supervision, Investigation, Conceptualization.

Declaration of competing interest

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

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Data availability

No data was used for the research described in the article.

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