Multiconfiguration electron density function for the
ATSP2K-package

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Abstract

A new \texttt{atsp2K} module is presented for evaluating the electron density function of any multi-
configuration Hartree-Fock or configuration interaction wave function in the non relativistic or
relativistic Breit-Pauli approximation. It is first stressed that the density function is not a priori
spherically symmetric in the general open shell case. Ways of building it as a spherical sym-
metric function are discussed, from which the radial electron density function emerges. This
function is written in second quantized coupled tensorial form for exploring the atomic spherical
symmetry. The calculation of its expectation value is performed using the angular momentum
theory in orbital, spin, and quasispin spaces, adopting a generalized graphical technique. The
natural orbitals are evaluated from the diagonalization of the density matrix.

Key words: Electron density, Density matrix, Natural orbitals, Multiconfiguration wave
functions

PACS: 31.15.-p, 31.15.ae, 31.15.V-, 31.15.xh, 45.10.Na

Program summary

Title of program: DENSITY ; version number: 1.00

Catalogue identifier:

Program obtainable from: CPC Program Library, Queen’s University
of Belfast, N. Ireland

Computers: HP XC Cluster Platform 4000
Installations: VUB-ULB Computer Center

Email addresses: mrgodef@ulb.ac.be (M. Godefroid)

Preprint submitted to Elsevier  July 16, 2009
Operating systems or monitors under which the present version has been tested: HP XC System Software 3.2.1, which is a Linux distribution compatible with Red Hat Enterprise Advanced Server.

Programming language used in the present version: FORTRAN 90

RAM: ?? MB or more

Peripherals used: terminal, disk

No. of bits in a word: 32

No. of processors used: 1

Has the code been vectorised or parallelized?: no

No. of bytes in distributed program, including test data, etc.: ?? bytes

Distribution format: gzipped compressed tar file

CPC Program Library subprograms used: libraries of atsr2K

Nature of physical problem
This program determines the atomic electronic density in the MCHF (LS) or Breit-Pauli (LS J) approximation. It also evaluates the natural orbitals by diagonalizing the density matrix.

Method of solution
Building the density operator using second quantization - Spherical symmetry averaging - Evaluating the matrix elements of the one-body excitation operators in the configuration state function (CSF) space using the angular momentum theory in orbital, spin, and quasispin spaces.

Restrictions on the complexity of the problem
Original restrictions from atsr2K package, i.e. all orbitals within a wave function expansion are assumed to be orthonormal. Configuration states are restricted to at most eight subshells in addition to the closed shells common to all configuration states. The maximum size of the working arrays, related to the number of CSFs and active orbitals, is limited by the available memory and disk space.

Typical running time
The calculation of the electron density for a $n = 9$ complete active space (CAS) MCHF wave function (271 733 CSFs - 45 orbitals) takes around 9 minutes on one AMD Opteron dual-core @ 2.4 GHz CPU.

Unusual features of the program
The programming style is essentially F77 with extensions for the POINTER data type and associated memory allocation. These have been available on workstations for more than a decade, but their implementations are compiler dependent. The present code has been installed and tested extensively using the Portland Group, pgf90, compiler.

References
1. “An MCHF atomic-structure package for large-scale calculation”, Charlotte Froese Fischer, Georgio Tachiev, Gediminas Gaigalas and Michel R. Godefroid, Computer Physics Communications 176 (2007) 559-579
1. Introduction

In electronic structure theory there are several approaches to describe the behavior of electrons in atoms and molecules. Most of them are based on the wave nature of the particles, permitting the system to be described by wave functions, as eigenstates of the Schrödinger equation. The Hohenberg–Kohn (HK) [1] theorems on the other hand say that the electronic structure of a system is completely determined by its ground state electron density function. According to the HK theorems, the energy of any system can be written as a functional of this density function. Based on these results, within Density Function Theory (DFT), several methods have been developed to describe atoms and molecules through their density function [2]. The development of density functionals which yield a system’s energy has become a major field of research in Chemistry and Physics. Nowadays a lot of research is being done to investigate how the electron density function describes the system. In conceptual DFT for example, chemical reactivity indices are defined, which indicate how a system behaves in a chemical reaction, by considering perturbations to the electron density function. Although wave function methods were well developed before, DFT is now the most widely used electronic structure method. The wide spread use of DFT can be accounted to the relative computational ease with which energies can be determined. Where a wave function describing an \( N \)-particle system involves the position- and spin- coordinates of all electrons, a density function, describing the same system, only depends on the coordinates of one particle. Following the work of McWeeny [3], one can try to extract physically essential features from the electron density function.

Some of the present authors have established the periodicity of the atoms in Mendeleev’s periodic Table by making an information theoretical analysis of the electron density functions as probability distributions [4]. Another work quantifies the relativistic effects on the basis of a comparison of density functions calculated within the one-configuration Hartree–Fock and Dirac–Fock approximations [5].

The present code is an extension of the Atomic Structure Package \texttt{atsp2K} [6] for evaluating the atomic density function from non relativistic and relativistic (in the Breit-Pauli approximation) multiconfiguration \textit{ab initio} wavefunctions of atomic systems, adopting an efficient approach for spin-angular integrations [7, 8]. It allows the investigation of correlation effects on the density function for any non-relativistic correlation model, and of relativistic effects in the Breit-Pauli approximation.
In quantum chemistry, the natural orbitals (NO) are known to provide a particularly efficient choice of single-particle states [9, 10]. Moreover, NO give the most rapidly convergent approximation to the total wave function and are often used as a basis set for generating a better wave function in an iterative manner. In atomic physics, NO are rarely used, although they constitute the orbital basis of the reduced form of the MCHF expansions for helium-like and nominal two-electron atomic systems [11]. It would be worthwhile to study their potential for more than two electrons in the search of efficient optimization strategies. The present code fills this gap by building the natural orbitals through the diagonalization of the density matrix.

2. On the symmetry of the density function

In this section we start by formulating the multiconfiguration wave function for a well defined atomic state, and we calculate the corresponding density function. From this calculation, we regain the specific angular (non-spherical) dependence of the density function. We also present different ways for deriving a spherical electron density function.

2.1. The multiconfiguration many-electron wavefunction

In the multiconfiguration approach, the \( N \)-electron wavefunction \( \Psi_{\alpha L S M_L M_S} \) is a linear combination of \( M \) configuration state functions (CSFs) \( \Phi_{\alpha L S M_L M_S} \) which are eigenfunctions of the total angular momentum \( L^2 \), the spin momentum \( S^2 \) and their projections \( L_z \) and \( S_z \), with eigenvalues \( \hbar^2 (L + 1) \), \( \hbar^2 (S + 1) \), \( hM_L \) and \( hM_S \), respectively

\[
\Psi_{\alpha L S M_L M_S} (\mathbf{x}_1, \cdots \mathbf{x}_N) = \sum_{i=1}^{M} c_i \Phi(\alpha_i; L S M_L M_S; \mathbf{x}_1, \cdots \mathbf{x}_N). \tag{1}
\]

The set of variables \( \{\mathbf{x}_j\} \) represent the electron’s space and spin coordinates \( \mathbf{x}_j = (r_j, \sigma_j) \equiv (r_j, \vartheta_j, \phi_j, \sigma_j) \). The individual CSFs are built from a set of one-electron spin-orbitals,

\[
\psi_{nlm,sm} (\mathbf{x}) = R_{nl}(r)Y_{lm}(\vartheta, \phi)\chi_{sm}(\sigma) = \frac{1}{r} P_{nl}(r)Y_{lm}(\vartheta, \phi)\chi_{sm}(\sigma), \tag{2}
\]

where \( R_{nl}(r) \equiv P_{nl}(r)/r \), \( Y_{lm}(\vartheta, \phi) \) and \( \chi_{sm}(\sigma) \) are the radial, the angular and the spin parts of the one electron functions. The mixing coefficients \( \{c_i\} \) and the radial functions \( \{R_{nl}(r)\} \) are solutions of the multiconfiguration Hartree-Fock method in the MCHF approach. For a given set of orbitals, the mixing coefficient may also be the solution of the configuration interaction (CI)
problem. The relativistic corrections can be taken into account by diagonalizing the Breit-Pauli Hamiltonian \[12\] in the $LSJ$-coupled CSF basis to get the intermediate coupling eigenvectors

$$\Psi_{\alpha JM}(x_1, \ldots, x_N) = \sum_{i=1}^{M'} a_i \Phi(\alpha, L_i S_i J M; x_1, \ldots, x_N). \quad (3)$$

2.2. The non-spherical density function

The so-called “generalized density function” \[3\] or the “first order reduced density matrix” \[13\] is a special case of the reduced density matrix \[10, 3\]

$$\gamma_1(x_1, x_1') = N \int \Psi(x_1, x_2, \ldots, x_N) \Psi^*(x_1', x_2, \ldots, x_N) \, dx_2 \ldots dx_N, \quad (4)$$

where $\Psi(x_1, x_2, \ldots, x_N)$ is the total wave function of an $N$ electron system and $\Psi^*(x_1, x_2, \ldots, x_N)$ is its complex conjugate. The spin-less total electron density function $\rho(r)$ is defined as the first order reduced density matrix, integrated over the spin and evaluated for $x_1 = x_1'$

$$\rho(r_1) = \int \gamma_1(x_1, x_1) d\sigma_1. \quad (5)$$

This electron density function is normalized to the number of electrons of the system

$$\int \rho(r) \, dr = \int \rho(r) \, r^2 \sin \theta dr d\theta d\phi = N. \quad (6)$$

As discussed in \[13\], the single particle density function can be calculated by evaluating the expectation value of the $\delta(r)$ operator,

$$\rho(r) = \int \Psi(x_1, x_2, \ldots, x_N) \, \delta(r) \, \Psi^*(x_1, x_2, \ldots, x_N) \, dx_1 dx_2 \ldots dx_N, \quad (7)$$

where $\delta(r)$ probes the presence of electrons at a particular point in space and can be written as the one-electron first-quantization operator

$$\delta(r) = \sum_{i=1}^{N} \delta(r - r_i). \quad (8)$$

Expressing each $\delta(r - r_i)$ term in spherical coordinates \[14\]

$$\delta(r - r_i) = \frac{1}{r^2 \sin \theta} \, \delta(r - r_i) \, \delta(\theta - \theta_i) \, \delta(\varphi - \varphi_i), \quad (9)$$

and introducing the closure relation

$$\sum_{l m} Y_{lm}(\theta, \varphi) Y_{lm}^*(\theta', \varphi') = \delta(\cos \theta - \cos \theta') \, \delta(\varphi - \varphi'), \quad (10)$$
the operator (8) becomes

$$\delta(r) = \sum_{i=1}^{N} \delta(r - r_i) = \frac{1}{r} \sum_{i=1}^{N} \left[ \delta(r - r_i) \sum_{lm} Y_{lm}(\theta_i, \varphi_i) Y_{lm}^*(\theta_i, \varphi_i) \right].$$  (11)

The exact spin-less total electron density function (7) evaluated for an eigenstate with well-defined quantum numbers \((LS M_L M_S)\), is

$$\rho(r)_{LS M_L M_S} = \sum_{lm} Y_{lm}(\theta, \varphi) \frac{1}{r} \langle \Psi_{aLS M_L M_S} \vert \sum_{i=1}^{N} \delta(r - r_i) Y_{lm}^*(\theta_i, \varphi_i) \rangle \vert \Psi_{aLS M_L M_S} \rangle$$  (12)

It is important to realize that the spherical harmonic components are limited to the \(l\)-even contributions, since the bra and ket states have the same parity \(\pi = (-1)^L \). Applying the Wigner-Eckart theorem [15] gives

$$\rho(r)_{2L}^{LS M_L M_S} = \sum_{l=0}^{2L} Y_{2l}(\theta, \varphi) \frac{1}{r} (-1)^{L-M_L} \left[ L \atop -M_L \right] \left( L \atop 0 \right) \langle \Psi_{aLS} \vert \sum_{i=1}^{N} \delta(r - r_i) Y_{2l}^*(\theta_i, \varphi_i) \rangle \vert \Psi_{aLS} \rangle$$  (13)

where

$$\rho(r)_{2l}^{LS M_L M_S} = \frac{1}{r} (-1)^{L-M_L} \left[ L \atop -M_L \right] \left( 2l \atop 0 \right) \langle \Psi_{aLS} \vert \sum_{i=1}^{N} \delta(r - r_i) Y_{2l}^*(\theta_i, \varphi_i) \rangle \vert \Psi_{aLS} \rangle.$$  (14)

This result recovers Fertig and Kohn’s analysis [17] for the density corresponding to a well-defined \((LS M_L M_S)\) eigenstate of the Schrödinger equation. In this paper, the authors observed that the self-consistent field densities obtained via the Hartree and Hartree-Fock methods generally violate the specific finite spherical harmonic content of \(\rho(r)_{LS M_L M_S}^{LS M_L M_S}\). They also mention that this exact form can be obtained by spherically averaging the effective potential, yielding single-particle states with good angular momentum quantum numbers. The atomic structure software package asep2K [6] applies this approach, as was done in the original atomic Hartree-Fock theory [13, 19, 11]. This implies two things: i) the density function \(\rho(r)_{LS M_L M_S}^{LS M_L M_S}\) calculated from any multiconfiguration wave function of the form (1), is not \emph{a priori} spherically symmetric, ii) this density function will contain all spherical harmonic components (up to 2\(L\)) as long as the one-electron orbital active set spanning the configuration space is \(l\)-rich enough.

\[1\] The same result can be obtained by reducing the many-electron reduced matrix element as a sum over one-electron reduced matrix elements as done in [16].
The density function can also be expressed in second quantization [3]. Introducing the notation \( q \equiv n_p l_m m_q \) for spin-orbitals, expression (4) becomes

\[
\gamma_1(x_1, x'_1) = \sum_{pq} D_{pq} \psi_p^*(x'_1) \psi_q(x_1),
\]

(15)

where \( D_{pq} \) are elements of the density matrix which are given by

\[
D_{pq} \equiv \langle \Psi | a_p^\dagger a_q | \Psi \rangle.
\]

(16)

The sum in eq. (15) runs over all possible pairs of quartets of quantum numbers \( p \) and \( q \). The spin-less density function [5] calculated from \( \rho(r) = \langle \Psi | \hat{\delta}(r) | \Psi \rangle \), using the second quantized form of the operator [3],

\[
\hat{\delta}(r) = \sum_{pq} a_p^\dagger a_q \delta_{m_p m_q} \langle \psi_p(r') | \frac{1}{r} \sin \theta \delta(r - r') \delta(\theta - \theta') \delta(\varphi - \varphi') | \psi_q(r') \rangle,
\]

(17)

yields

\[
\rho(r) = \sum_{pq} D_{pq} \delta_{m_p m_q} R_{n_p l_p q}^r \psi_{l_p m_p}^*(\theta, \varphi) R_{n_q l_q q}^r \psi_{l_q m_q}^r(\theta, \varphi).
\]

(18)

To illustrate the spherical harmonics content of the density in the Hartree-Fock approximation, consider the atomic term \( 1s^2 2p^2 (3p) 3d^4 F \) for which the \( (M_L, M_S) = (+3, +3/2) \) subspace reduces to a single Slater determinant

\[
\Psi_{aLSM_L M_S} = \Phi(1s^2 2p^2 (3p) 3d^4 F_{+3, +3/2}) = \big| 1s^1 2p_{+1} 2p_{0} 3d_{+2} \big|.
\]

(19)

When evaluating (18), all non-zero \( D_{pq} \)-values appear on the diagonal \( (p = q) \), yielding

\[
\rho(r)^{F_{+3, +3/2}} = |\psi_{1s}(r)|^2 + |\psi_{2p_{+1}}(r)|^2 + |\psi_{2p_{-1}}(r)|^2 + |\psi_{3d_{+2}}(r)|^2.
\]

(20)

This density has a clear non-spherical angular dependence. However, referring to (20),

\[
W_{JM}^\Lambda(\theta, \varphi) = |Y_{JM}(\theta, \varphi)|^2 = \sum_{n=0}^J b_n(J, M) P_{2n}(\cos \theta) \sum_{\pm} b_n'(J, M) Y_{2n0}(\theta, \varphi)
\]

(21)

one recovers the even Legendre polynomial content of the density, although not reaching the \((2L = 6)\) limit \( Y_{60}(\theta, \varphi) \) of the exact density [13]. However this limit will be attained when extending the one-electron orbital active set to higher angular momentum values for building a correlated wave function.
Mixed contributions \((p \neq q)\) may appear in \((18)\) through off-diagonal matrix elements in the CSF basis. For example, the interaction of \(\Phi(1s^22p^2(\;^3P)3d^4F_{3,3/2})\) with the angular correlation component \(\Phi(1s^22p3d(\;^3F)4f^4F_{3,3/2})\), a single electron excitation \(2p \rightarrow 4f\), gives rise to \(Y_{10}^* Y_{30}\) and \(Y_{1+1}^* Y_{3+1}\) contributions. But these contributions are also limited to even Legendre polynomials, as appearing in equation \((13)\). Indeed, starting from the Clebsch-Gordan series \([20]\)

\[
Y_{l,m_l}(\theta, \varphi) Y_{l',m'_l}(\theta, \varphi) = \sum_{l''=|l_l-l'_l|}^{l_l+l'_l} \sum_{m''=l''-l_l}^{l''+l_l} \left[ \frac{(2l_1 + 1)(2l_2 + 1)(2l + 1)}{4\pi} \right]^{1/2} (-1)^m \begin{pmatrix} l_1 & l_2 & l \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_1 & l_2 & l \\ m_1 & m_2 & -m \end{pmatrix} Y_{m''}(\theta, \varphi) \tag{22}
\]

and using

\[
Y_{l-m}(\theta, \varphi) = (-1)^m Y_{l+m}(\theta, \varphi), \tag{23}
\]

one finds that any contribution of the type \(Y_{i,q}^* Y_{i,q}\) arising from a single electron excitation \(|l_1q\rangle \rightarrow |l_2q\rangle\) preserving the parity, i.e. \((-1)^{l_1} = (-1)^{l_2}\), takes the form

\[
Y_{i,q}^* (\theta, \varphi) Y_{i,q}(\theta, \varphi) = (-1)^q \sum_{l''=|l_l-l'_l|}^{l_l+l'_l} \left[ \frac{(2l_1 + 1)(2l_2 + 1)(2l + 1)}{4\pi} \right]^{1/2} \begin{pmatrix} l_1 & l_2 & l \\ 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} l_1 & l_2 & l \\ -q & +q & 0 \end{pmatrix} Y_{m''}(\theta, \varphi). \tag{24}
\]

At this stage, we would like to stress that in an MCHF calculation the density never contains – what Fertig and Kohn \([17]\) called – “offending” spherical harmonic components, whatever the maximum \(l\)-value of the orbital active space.

2.3. The spherical density function

A spherically symmetric density function can be obtained for an arbitrary CSF \(\Phi_{aLSM_1M_3}\) by averaging the \((2L + 1)(2S + 1)\) magnetic components of the spin-less density function

\[
\rho(r)^{LS} = \frac{1}{(2L + 1)(2S + 1)} \sum_{M_1M_3} \rho(r)^{LSM_1M_3}, \tag{25}
\]

where \(\rho(r)^{LSM_1M_3}\) is constructed according to eq. \((18)\)

\[
\rho(r)^{LSM_1M_3} = \sum_{pq} \langle \Phi_{aLSM_1M_3} | a^\dagger_p a_q | \Phi_{aLSM_1M_3} \rangle \: \delta_{m_p m_q} \: \psi^*_p(r) \psi_q(r). \tag{26}
\]

Applying equations \((25)\) and \((26)\) for the atomic term \(1s^22p^2(\;^3P)3d^4F\) considered in the previous section, we simply get

\[
\rho(r)^{4F} = \frac{1}{4\pi r^2} \left\{ 2P_{11}^2(r) + 2P_{2p}^2(r) + P_{3d}^2(r) \right\}. \tag{27}
\]
which is, in contrast to eq. (20), obviously spherically symmetric. The sum over \((M_L, M_S)\) performed in (25) guarantees, for any nl-subshell, the presence of all necessary components \(\{Y_{l0} | m_l = -l, \ldots, +l\}\) with the same weight factor, which permits the application of Unsöld’s theorem \[21\]

\[
\sum_{m_l = -l}^{+l} |Y_{lm}(\theta, \varphi)|^2 = \frac{2l + 1}{4\pi} 
\]

and yields the spherical symmetry. This result is valid for any single CSF

\[
\rho(r)^{L_S} = \frac{1}{4\pi r^2} \sum_{nl} q_{nl} r^2 P_{nl}(r) ,
\]

where \(q_{nl}\) is the occupation number of \(nl\)-subshell. Its sphericity explicitly appears by rewriting \(29\) as

\[
\rho(r) = \rho(0) |Y_{00}(\theta, \varphi)|^2 = \frac{D(r)}{r^2} |Y_{00}(\theta, \varphi)|^2 ,
\]

with

\[
\rho(r) = \frac{1}{r^2} \sum_{nl} q_{nl} r^2 P_{nl}(r) ,
\]

and

\[
D(r) \equiv r^2 \rho(r) = \sum_{nl} q_{nl} r^2 P_{nl}(r) = \sum_{nl} q_{nl} r^2 R_{nl}(r) .
\]

The radial distribution function \(D(r)\) represents the probability of finding an electron between the distances \(r\) and \(r + dr\) from the nucleus, regardless of direction. This radial density function reveals the atomic shell structure when plotted as function of \(r\). Its integration over \(r\) gives the total number of electrons of the system

\[
\int_0^\infty D(r) \, dr = \int_0^\infty r^2 \rho(r) \, dr = \sum_{nl} q_{nl} = N .
\]

Where above the spherical symmetry of the average density \(25\) is demonstrated for a single CSF thanks to Unsöld’s theorem, it can be demonstrated in the general case by combining \(25\), \(13\) and the 3-\(j\) sum rule \[15\]

\[
\sum_{M_L} (-1)^{L-M_L} \begin{pmatrix} L & k & L \\ -M_L & 0 & M_L \end{pmatrix} = (2k + 1)^{1/2} \delta_{k,0}
\]

Note that, although denoted as \(D\), this function (evaluated at the \(r = 0\)) is not the so-called “modified electron density” used in the context of isotope shifts \[22\]. The latter is indeed \(\rho(0) = 4\pi \rho(0)\).
for each \( k = 2l \) contribution (14). However, the radial density \( \rho(r) \) will be more complicated than (31), involving mixed contributions of the type \( P_{n'f}(r)P_{mf}(r) = r^2R_{n'f}(r)R_{mf}(r) \), as developed below.

Instead of obtaining a spherically symmetric density function by averaging the magnetic components \( \rho(r)_{LSM,LMS} \) through eq. (25), one can build a radial density operator associated to the function (32) which is spin- and angular-independent, i.e. independent of the spin \( (\sigma) \) and angular \((\theta, \varphi)\) variables. Adopting the methodology used by Helgaker et al. [13] for defining the spin-less density operator, we write a general first quantization spin-free radial operator

\[
f = \sum_{i=1}^{N} f(r_i) \quad (35)
\]

in second quantization as

\[
f^\dagger = \sum_{pq} f_{pq} a^\dagger_p a_q , \quad (36)
\]

where \( f_{pq} \) is the one-electron integral

\[
f_{pq} = \int \psi_p(x)f(r)\psi_q(x)r^2 \sin\theta drd\theta d\varphi d\sigma . \quad (37)
\]

Applying this formalism to the radial density operator

\[
\delta(r) \equiv \sum_{i=1}^{N} \delta(r - r_i) , \quad (38)
\]

and using the spin-orbital factorization (2) for both \( p \) and \( q \) quartets, we obtain the second quantization form

\[
\hat{\delta}(r) = \sum_{pq} d_{pq}(r) a^\dagger_p a_q , \quad (39)
\]

with

\[
d_{pq}(r) = \delta_{l'l''} \delta_{m_p,m_q} \delta_{m_p,m_q} R_{n'l''}(r)R_{n'l}(r)r^2 , \quad (40)
\]

where the Kronecker delta arises from the orthonormality property of the spherical harmonics and spin functions. With real radial one-electron functions, the operator (39) becomes

\[
\hat{\delta}(r) = \sum_{n'l'n''l''mlmn} \delta_{l'l''} \delta_{m_l,m_{l'}} \delta_{m_{l'},m_{l''}} a^\dagger_{nl'm'} a_{nl'm''} R_{n'l''}(r)R_{n'l}(r)r^2 \quad (41)
\]

\[
= \sum_{n'l'n} \sum_{lm} a^\dagger_{nl'm} a_{nl'm} R_{n'l}(r)R_{n'l}(r)r^2 . \quad (42)
\]
its expectation value provides the radial density function \( D(r) = r^2 \rho(r) = 4\pi r^2 \rho(r) \) defined by (30) and (32).

Building the coupled tensor of ranks (00) from the \([2(2l+1)]\) components of the creation and annihilation operators [2,3]

\[
(a_{\alpha}^\dagger a_{\alpha})_{00}^{(00)} = -\frac{1}{\sqrt{2(2l+1)}} \sum_{m,n} a_{\alpha}^\dagger_{m,n} a_{n,m} ,
\]

the operator (41) becomes

\[
\hat{\rho}(r) = -\sum_{l} \sqrt{2(2l+1)} \sum_{n,n'} (a_{\alpha}^\dagger a_{\alpha})_{00}^{(00)} R_{n}(r) R_{n'}(r) r^2 .
\]

The expectation value of this operator provides the spherical density function for any atomic state. Note that, in contrast to (26), the tensorial ranks (00) guarantee the diagonal character in \(L, S, M_L\) and \(M_S\), thanks to Wigner-Eckart theorem

\[
\langle \alpha LS M_L M_S | T_{00}^{(00)} | \alpha' L'S' M'_L M'_S \rangle = (-1)^{L+S-M_L-M_S} \begin{pmatrix} L & 0 & L' \\ -M_L & 0 & M'_L \end{pmatrix} \begin{pmatrix} S & 0 & S' \\ -M_S & 0 & M'_S \end{pmatrix} \langle \alpha LS || T^{(00)} || \alpha' L'S' \rangle .
\]

Moreover, the \(M_L/M_S\) independence emerges from the special 3\(j\)-symbol

\[
\begin{pmatrix} j & 0 & j' \\ -m_j & 0 & m'_j \end{pmatrix} = (-1)^{-m}(2j+1)^{-1/2} \delta_{jj'} \delta_{m_m'} .
\]

In other words, where the non-spherical components are washed out by the averaging process (25), they simply do not exist and will never appear for the density calculated from (44), for any \((M_L, M_S)\) magnetic component.

The radial distribution function \( D(r) \equiv r^2 \rho(r) \) can be calculated from the expectation value of the operator (44), using the wave function (1) or (3). In the most general case (expansion (3)), using the \((LS)J\)-coupled form of the excitation operator,

\[
(a_{\alpha}^\dagger a_{\alpha})_{00}^{(00)} = (a_{\alpha}^\dagger a_{\alpha})_{00}^{(00)} ,
\]

one obtains

\[
\langle \Psi_{\alpha JM} | \hat{\rho}(r) | \Psi_{\alpha' JM} \rangle = (-1)^{l-M} \begin{pmatrix} J & 0 & J \\ -M & 0 & M \end{pmatrix} \langle \Psi_{\alpha J} || \hat{T}^{(00)} || \Psi_{\alpha J} \rangle .
\]
with
\[ \bar{F}_{p,0}^{(00)} = -\sum_{l=1}^{l_{\max}} \sqrt{2(2l+1)} \sum_{n,n'} (a_{m,n'}|a_{m,n})_{0}^{(00)} I_p(n',nl) , \]  
(49)

and
\[ I_p(n',nl)(r) \equiv R_{n',l}(r)R_{nl}(r)r^2 . \]  
(50)

The diagonal reduced matrix element (RME) evaluated with the Breit-Pauli eigenvector \( |\psi\rangle \) has the following form
\[ \langle \Psi_{a,l}||\bar{F}_{p}^{(00)}||\Psi_{a,l} \rangle = \sum_{i,j} a_{i}^{*}a_{j} \langle \Phi(\alpha_1,l_1S_1,J)||\bar{F}_{p}^{(00)}||\Phi(\alpha_1,l_1S_1,J) \rangle \]  
(51)

where the RME in the \( (LS)J \) coupled basis reduces to
\[ \langle \Phi(\alpha_1,l_1S_1,JM)||\bar{F}_{p}^{(00)}||\Phi(\alpha_1,l_1S_1,JM) \rangle = \sqrt{2J+1/(2L+1)(2S+1)} \langle \Phi(\alpha_1,l_1S_1)||\bar{F}_{p}^{(00)}||\Phi(\alpha_1,l_1S_1) \rangle \delta_{L,L'} \delta_{S,S'} , \]  
(52)

and
\[ \bar{F}_{p,00}^{(00)} = -\sum_{l=1}^{l_{\max}} \sqrt{2(2l+1)} \sum_{n,n'} (a_{m,n'}|a_{m,n})_{0}^{(00)} I_p(n',nl) . \]  
(53)

From the analogy of the operator \( \bar{F}_{p}^{(00)} \) and the non-relativistic one-body Hamiltonian operator (see eq. (A5) of \[24\]), one observes that the angular coefficients of the radial functions \( I_p(n',nl)(r) \) are identical to those of the one-electron Hamiltonian radial integrals \( I_{n',nl} \), as anticipated from McWeeny analysis \[3\]. These angular coefficients can be derived by working out the matrix elements of a one–particle scalar operator \( \bar{F}_{p}^{(00)} \) between configuration state functions with \( u \) open shells, as explicitly derived by Gaigalas et al \[25\] who expressed them as a sum over one–electron contributions
\[ \langle \Phi(\alpha LS)||\bar{F}_{p}||\Phi(\alpha' LS) \rangle = \sum_{n,l,n',l'} \langle \Phi(\alpha LS)||\bar{F}_{p}(n_l,l,n',l')||\Phi(\alpha' LS) \rangle \]  
(54)

where
\[ \langle \Phi(\alpha LS)||\bar{F}_{p}(n_l,l,n',l')||\Phi(\alpha' LS) \rangle = (-1)^{l+1} \sqrt{2(2l+1)} R(\lambda_1,\lambda_2,\Lambda^{br},\Lambda^{kr}) \delta_{L,L'} I_p(n_l,l,n',l') \]
\[ \times \left\{ \delta(n_l,n') \left[ n_{l'}^{N} \alpha_{l} Q_{l} L_{s} S_{i} \left[ d_{l/2}^{(q_{1} l_{i} s)} \times a_{l_{1} l_{2}}^{(q_{1} l_{i} s)} \right] \right] \left[ n_{l'}^{N} \alpha_{l} Q_{l} L_{s} S_{i} \right] \right\} \]
\[ \times \left\{ n_{l'}^{N} \alpha_{l} Q_{l} L_{s} S_{j} \left[ d_{l_{1} l_{2}}^{(q_{1} l_{i} s)} \right] \left[ n_{l'}^{N} \alpha_{l} Q_{l} L_{s} S_{j} \right] \right\} \]  
(55)
In this last expression, $\lambda \equiv l$ or $s$, $\langle \Phi(\alpha LS) |$ and $|\Phi(\alpha'LS) \rangle$ are respectively bra and ket functions with $u$ open subshells, $\Lambda_{\text{bra}} \equiv \left( L_S i, L_j S_j, L_{-j} S_{-j}, L_{-j'} S_{-j'} \right)^{\text{bra}}$ and $\Lambda_{\text{ket}} \equiv \left( L_S i, L_j S_j, L_{-j} S_{-j}, L_{-j'} S_{-j'} \right)^{\text{ket}}$ denote the respective sets of active subshell angular momenta. The operators $\hat{a}_{\ell m}^{(q\ell)}$ are second quantization operators in quasispin space of rank $q = 1/2$. The operator $\hat{a}_{l/2 m_l m_s}^{(q\ell)} = \hat{a}_{m_l m_s}^{(l)}$ creates electrons with angular momentum quantum numbers $l, m_l, s, m_s$ and its conjugate $\hat{a}_{1/2 m_l m_s}^{(q\ell)} = \hat{a}_{m_l m_s}^{(l)} = (-1)^{l_s r-m_l-m_s} \hat{a}_{r m_l m_s}^{(l)}$ annihilates electrons with the same quantum numbers $l, m_l, s, m_s$ in a given subshell. The coefficient $R(\lambda, \lambda', \Lambda_{\text{bra}}, \Lambda_{\text{ket}})$ is the recoupling matrices in $l$- and $s$- spaces and $\Delta$ is a phase factor.

3. Density matrix and natural orbitals

Using (43), (51), (52) and (55), the radial distribution function gets the following form

$$D(r) = r^2 \rho(r) = \sum_{i j} a_i^* D_{ij}(r) a_j = \sum_{i j} a_i^* \left[ \sum_{l} \sum_{n} v_{nl}^{ij} \rho_l(n', l, n) \right] a_j ,$$

which can be rewritten in a compact form

$$D(r) = \sum_{l} \sum_{n' n} \rho_{n' n}^l \rho_l(n', l, n) ,$$

with

$$\rho_{n' n}^l = \sum_{i j} c_i^* v_{nl}^{ij} a_j .$$

The $\delta_{l_i, l_j}$ Kronecker appearing in (55) assures the block-structure of the density matrix $\rho$ whose elements are defined by (58) for the $l$-angular symmetry.

The natural orbitals (NO) are defined as the one-electron functions that diagonalize the density matrix $\rho$

$$C^l \rho C = \tilde{\rho} .$$

Within a specific angular $l$-symmetry, the eigenvalue problem for the relevant $l$-block

$$\rho^l C^l = C^l \tilde{\rho}^l$$

defines the natural radial orbitals through the following transformation

$$\tilde{R}_k(r) = \sum_n c_n^l R_n(r) .$$

The eigenvalues $\{ \lambda'_k = \tilde{\rho}_{kk}^l \}$ are interpreted as the occupation numbers of the NOs $\{ \tilde{R}_k(r) \}$.
4. Algorithm description

To calculate the radial density function and the natural orbitals from an arbitrary $N$-electron wavefunction $\Psi_{a JM}$, we wrote a FORTRAN implementation of equation (48), as an extension of the atm2K package. The essential part in the calculation of the density function, is the evaluation of the reduced matrix element (51). In pseudo-code, the reduced matrix element (51) is written as

$$
\langle \Psi_{\alpha J} | \hat{F}^{(00)} \rho | \Psi_{\alpha J} \rangle = \sum_i \sum_j a_{iJ} \sum_{\mu} \sum_{\nu} I_{\rho}(\mu, \nu) \text{UNITELEMENT}(\mu, \nu)
$$

$$
\text{SPIN\_ANGULAR\_DENSITY}(\text{CSF}_i, \mu; \text{CSF}_j, \nu; 00) . \quad (62)
$$

where

$$
\text{UNITELEMENT}(\mu, \nu) = -[l_{\mu}, s_{\mu}]^\dagger \delta(l_{\mu}, l_{\nu}) . \quad (63)
$$

The routine SPIN\_ANGULAR\_DENSITY, is inspired by the routine NONHIPER of the hfs hyperfine structures program of ATSP2K. It organizes the calculation of the spin-angular part of (55) by calling the subroutine ONEPARTICLE1 or ONEPARTICLE2 from [6]. ONEPARTICLE1 performs the calculation of the spin-angular part when the one-electron operator acts on one open shell and ONEPARTICLE2 performs the calculation when the operator acts on two open shells. Both calculate the spin-angular part using the expression (55) in which $I_{\rho}(n_i l_i, n_j l_j) = 1$. The products of the weight factors with the corresponding spin-angular part are stored and accumulated in the two dimensional array FACTORMATRIX($\mu$, $\nu$) where the rows and columns are defined by the ($nl$) subshell quantum numbers of the bra and ket, respectively. FACTORMATRIX is the precursor of the density matrix (58). The products of the array elements with their corresponding radial part $I_{\rho}(n'l', nl)$ are accumulated to build the radial distribution function (57). The reader is referred to the flowchart in figure[1] for a schematic overview of the calculation of the density function.

The NOs are obtained by diagonalizing this matrix and using the eigenvectors to construct the orbitals. The diagonalization of the density matrix (59) is performed using the DSYEV subroutine from the Lapack [26] library. This routine computes all eigenvalues and eigenvectors for a given real symmetric matrix. The NOs are ordered and labelled according to their occupation numbers $\{l^j_k = \rho^j_{kk}\}$. 

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Most of the subroutines needed for density exist in hfs of ATSP2K, besides the routines from the ATSP2K libraries. The new modules are density.f, spin_angular_density.f and unitelement.f. The code readwfn.f that reads in the wave functions differs from the one encountered in hfs by the COMMON/ADATA2/AT,TT,ELNAME(NWD) needed to store the ATOM, TERM and ELNAME variables.

As an illustration, an interactive session is described in appendix A for a $n = 3$ CAS-MCHF expansion of the beryllium ground state (63 CSFs). Upon execution of density, the user is asked to specify the name of the data files, which were obtained from an ATSP2K run. density then reads the CSF weights ($\{c_i\}$ and $\{a_i\}$ for the non-relativistic and Breit-Pauli expansions, respectively), the configuration state functions quantum numbers and the radial functions from the files. The conventions of the data and the file types, summarized in table I were adopted from ATSP2K. However, for a relativistic calculation, the $\cdot$.j should be renamed file $\cdot$.l and edited to extract the selected relativistic $J$-eigenvector of interest.

In an interactive session, density asks the user a few questions concerning the output and whether the NOs should be evaluated. In table we list and comment the questions. Most of the output, however, is written to disk. The output files produced by the program are summarized in table 3. The name.d file, which is always generated, contains the radial distribution $D(r)$ and density $\rho(r)$ functions. The density program by default generates some output to the standard out: the “modified electron density” $[22]$ at the nucleus ($\rho(0) = 4\pi\rho(0)$), the occupation numbers of the natural orbitals, with their composition in terms of the original orbitals, and as a final check, the integral of the density function that should give the total number of electrons according to $[33]$. The $P_{nl}(\rho)$ and $P_{nl}(\rho)$ functions appearing in the files name.plt and name.n are defined in the logarithmic variable $\rho = \log_e(Zr)$ $[11]$ for the original and natural orbitals respectively. If the user asks for more details (‘yes’ to the question PRINT ALL DATA (y/*)), density prints out the contributions to the reduced matrix element $[62]$, providing for each pair $(i, j)$ of CSFs, the labels $(\mu, \nu)$ of the orbitals involved, the corresponding spin-angular coefficient, together with the relevant weights product ($a_i a_j$). Using this option, the user also gets the contributions to the modified density at the nucleus, the norm of the input orbitals, the matrix elements of the density matrix, and the natural orbitals (before they are sorted according to their occupation number), with their complete eigenvector composition.

To install the program (FORTRAN 90 compilation and linking with the ATSP2K libraries),
the provided INSTALL script should be edited to set the appropriate path and environment variables.

5. Applications and examples

To illustrate the data in the output files, we plotted in figure 2 the radial density distribution
\[ D(r) = r^2 \rho(r) \]
from the .d output file calculated for a CAS-MCHF wave function of the beryllium ground state (Be \( 1s^22s^2\,1S \)), using a \( n = 9 \) orbital active set. In the same figure, the Hartree-Fock radial density is compared with the one obtained with two correlation models: i) the \( n = 2 \) CAS-MCHF expansion, largely dominated by the near-degeneracy mixing associated to the Layzer complex \( 1s^2(2s^2 + 2p^2) \) and ii) the \( n = 9 \) CAS-MCHF. From the plotted results we notice that the density of the \( n = 2 \) calculation already contains the major correlation effects, compared to the \( n = 9 \) calculation. Indeed, the density does not seem to change a lot by going from the \( n = 2 \) to the \( n = 9 \) orbital basis, the valence double excitation \( 1s^22p^2 \) contributing for 9.7% of the wave function. From the energy point of view however, this observation is somewhat surprising (see table 4): the correlation energy associated to the \( n = 2 \) CAS-MCHF solution “only” represents 47% of the \( n = 9 \) correlation energy.

In a separated pair-MCHF approach, the reduced forms of the CSF expansions are often used to get a compact multiconfiguration representation of the state and to avoid possible variational redundancies between orbital rotations and mixing coefficients transformations. For some specific cases, the so-produced MCHF one-electron functions are nothing else than the natural orbitals [11]. For expansions closed under orbital rotations, one can test our density computational tool by: 1) performing an (unreduced) MCHF calculation, 2) obtain the natural orbitals from the diagonalization of the density matrix and 3) making a CI calculation in the resulting NO basis. Both calculations should yield the same total energy for two rather different representations of the same total wave function. Amongst the two, the NO-CSF expansion is naturally condensed. This is illustrated in table 5 for a \( n = 5 \) SD-MCHF valence correlation calculation on the ground state of Be \( (E = -14.619\,083 \text{ a.u.}, \text{ using a Hartree-Fock frozen core}) \). The eigenvectors calculated in both MCHF and NO one-electron bases are reported and compared to each other. Note that, in this specific case (a pair of \( 1S^\pi \) symmetry), the transformation that diagonalizes the density matrix eliminates the off-diagonal \( (n \neq n') \) contributions \( 1s^2nln'l' \) [27]. The reduction in the number of CSFs (30 \( \rightarrow \) 15) through the use of NOs is quite impressive. For a \( n = 6 \) SD-MCHF valence correlation calculation the CI-NO approach yields a CSF expansion with 29 terms less
and for a CAS-MCHF \( n = 9 \) wave function (271,733 CSFs), the NO basis leads to a reduction of 15,695 CSFs.

As a third example, we illustrate the influence of relativistic effects – in the Breit-Pauli approximation – on the density function of the Be-like \( \text{O}^{+4} \) atom, by comparing the densities of the fine-structure states \( 1s^2 2s 2p \, ^3P^0, \, ^3P^1 \) and \( ^3P^2 \). From the plots in figure 3 and the data given in table 6 we observe that the largest energy difference corresponds to the largest difference in density function. More bound is the level, higher is the electron density in the inner region.

When studying the electron affinities, it is often interesting to investigate the differential correlation effects between the negative ion and the neutral system [28]. Figure 4 displays the density functions \( D(r) \) of both the \([\text{Ne}]3s^2 3p^4 \, ^3P \) ground state of neutral Sulphur (S) and the \([\text{Ne}]3s^2 3p^5 \, ^2P^o \) ground state of the negative ion \( \text{S}^- \), evaluated with elaborate correlation models [29], together with their difference \( \Delta D(r) \). The latter reveals where the “extra” electron lies and its integration gives one, as it should.

Acknowledgements

The authors acknowledge Thomas Carette, Paul Geerlings and Brian Sutcliffe for helpful discussions. M. Godefroid thanks the Communauté française of Belgium (Action de Recherche Concertée) and the Belgian National Fund for Scientific Research (FRFC/IISN Convention) for financial support.

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A. An interactive session

$cat n3.c

1s( 2) 2s( 2)
1s 1s 1s
1s( 2) 2s( 1) 3s( 1)
1s 2S 1S 1S
1s( 2) 2p( 2)
1s 1S 1S
1s( 2) 2p( 1) 3p( 1)
1s 2P 1P 1P
1s( 2) 3s( 2)
1s 1S 1S
1s( 2) 3p( 2)
1s 1S 1S
1s( 2) 3d( 2)
1s 1S 1S
1s( 1) 2s( 2) 3s( 1)

$cat n3.l

Be Z = 4.0 NEL = 0 NCFG = 63

2*J = 0 NUMBER = 1
Sums = 0.484179758
1 -14.654414586 1s(2).2s(2)_1S
0.95181933 0.00029779 0.30027819 0.00037936-0.00118903-0.00023749-0.01763502
0.00019391-0.04365498 0.00316223-0.00663489 0.003776768-0.00043175 0.00173694
-0.00032836-0.00086628 0.00002903 0.00159570-0.00108079-0.00181964 0.00002085
-0.00001498-0.00000941 0.00415462 0.00703251-0.02349037 0.02848932-0.00012045
-0.00265663 0.00007304-0.00016224-0.00019179 0.00009463 0.00016368 0.00001426
0.00011178-0.00039979 0.00061770 0.00194285-0.00725367-0.0000453 0.00897260
Density calculation, Summer 2009

Give <name> of the <name>.c, <name>.l <name>.w files:

Files: n3

PRINT THE ORBITALS (*/n)
Print out orbitals

PRINT THE MATRIX (*/n)
Print out the matrix

CALCULATE NATURAL ORBITALS (*/n)
Calculate natural orbitals

PRINT ALL DATA (y/*)
Do not print all informations

ANALYSING THE CALCULATION

----------------------------
ACCURACY IS SET TO 1.0000000000000007E-016

STATE (WITH 63 CONFIGURATIONS):

THERE ARE 6 ORBITALS AS FOLLOWS:

1s 2s 2p 3s 3p 3d

THERE ARE 0 CLOSED SUBSHELLS COMMON TO ALL CONFIGURATIONS AS FOLLOWS:

NORM OF WEIGHTS = 1.000000004562740

ATOM Be  TERM 1sE

ALL WAVEFUNCTIONS EXIST.

START OF THE DENSITY CALCULATION

MODIFIED ELECTRON DENSITY AT THE NUCLEUS:
D = 444.31734212383130000

EIGENVECTOR:

1 = Eigenvalue 6 : 0.19968596313710157E+01
1s '=
-0.99450714610441153E+00 1s AZ= 0.14887071657598840E+00
0.104660655081394691E+00 2s AZ= 0.1019465194727872E+01
-0.94819357413400507E-04 3s AZ= 0.23772474518338814E+02

2 = Eigenvalue 5 : 0.181477021415131498E+01
2s '=
0.9945071235440736E+00 2s AZ= 0.1019465194727872E+01
0.104686296057672E+00 1s  AZ= 0.1488707165759884E+02
0.2433400492505317E-03 3s  AZ= 0.2377247451833881E+02

3 = Eigenvalue 2 : 0.1250344482753356E-02
3s =
0.999996589623770E+00 3s  AZ= 0.2377247451833881E+02
-0.1197691254232996E-03 1s  AZ= 0.1488707165759884E+02
-0.23208377825771107E-03 2s  AZ= 0.1019465194727872E+01

4 = Eigenvalue 4 : 0.1845862963217419E+00
2p =
-0.99999853877956664E+00 2p  AZ= 0.1505731981228271E+01
-0.1709514798808027E-02 3p  AZ= 0.5188118692894328E+02

5 = Eigenvalue 3 : 0.1899347338252901E+02
3p =
-0.99999653877956664E+00 3p  AZ= 0.5188118692894328E+02
-0.1709514798808027E-02 2p  AZ= 0.1505731981228271E+01

6 = Eigenvalue 1 : 0.6343112754478998E-03
3d =
0.1000000000000000E+01 3d  AZ= 0.31738718272621771E+00

SUM OF EIGENVALUES 4.000000018250960

INTEGRAL OF THE DENSITY FUNCTION:
N = 4.000000018250960

DENSITY FUNCTION IS IN FILE n3.d
END.
extension | data in the file
--- | ---
.c | configuration state function (CSF) expansion
.w | radial wave functions (numerical values in binary form)
.l | expansion coefficients from a non-relativistic (LS) calculation
.j | expansion coefficients from a Breit-Pauli (LS J) calculation

Table 1: File convention

| Question | Answer | Implication |
| --- | --- | --- |
| PRINT THE ORBITALS */n | y | The input radial functions will be written to .plt. |
| PRINT THE MATRIX */n | y | The density matrix will be written to .matrix. |
| CALCULATE NATURAL ORBITALS */n | y | Calculate the NOs and write them on .n (formatted) and .nw (unformatted) files. |
| PRINT ALL DATA y/* | y | Detailed output written to std out: MODIFIED DENSITY AT THE NUCLEUS NORM OF THE ORBITALS DENSITY MATRIX EIGENVALUES AND EIGENVECTORS |

Table 2: Questions density asks the user. "*" indicates the default answer.

extension | data in the file
--- | ---
.plt | \( r_i, R_{nl}(r_i), \bar{P}_{nl}(r_i) = r_i R_{nl}(r_i), \bar{P}_{nl}(\rho_i) = r_i^{\frac{3}{2}} \bar{P}_{nl}(r_i) \)
.d | \( r_i, \rho(r_i), D(r_i) = r_i^2 \rho(r_i) \)
.n | \( r_i, \bar{R}_{nl}(r_i), \bar{P}_{nl}(r_i) = r_i \bar{R}_{nl}(r_i), \bar{P}_{nl}(\rho_i) \) for Natural Orbitals
.nw | analogue of .w for the Natural Orbitals (contains \( \bar{P}_{nl}(\rho_i) \))

Table 3: Output files created by density

| model | energy (a.u.) | correlation energy (a.u.) |
| --- | --- | --- |
| HF | -14.573 023 |  |
| \( n = 2 \text{-CAS} \) | -14.616 856 | \( E^{n=2} - E^{HF} = 0.043 832 \) |
| \( n = 9 \text{-CAS} \) | -14.667 013 | \( E^{n=9} - E^{HF} = 0.093 986 \) |

Table 4: Total energy for the ground state of Be with different correlation models.
| CSF  | MCHF basis  | Natural orbital basis |
|------|-------------|-----------------------|
| 1s(2) 2s(2) | 0.95282855 | 0.95370264 |
| 1s(2) 2s(1) 3s(1) | 0.03858929 | 0.00000000 |
| 1s(2) 2s(1) 4s(1) | -0.01524193 | 0.00000000 |
| 1s(2) 2s(1) 5s(1) | 0.00133387 | -0.00000001 |
| 1s(2) 2p(2) | 0.00133387 | 0.29736974 |
| 1s(2) 2p(1) 3p(1) | -0.00032489 | 0.00000000 |
| 1s(2) 2p(1) 4p(1) | -0.00019862 | 0.00000000 |
| 1s(2) 2p(1) 5p(1) | 0.00089172 | -0.00000001 |
| 1s(2) 3s(2) | -0.03930620 | -0.0431077 |
| 1s(2) 3s(1) 4s(1) | -0.00463218 | 0.00000000 |
| 1s(2) 3s(1) 5s(1) | 0.00091733 | 0.00000000 |
| 1s(2) 3p(2) | 0.29736945 | 0.00532217 |
| 1s(2) 3p(1) 4p(1) | -0.0003969 | 0.00000000 |
| 1s(2) 3p(1) 5p(1) | 0.00024549 | 0.00000000 |
| 1s(2) 4s(2) | -0.00422002 | -0.00432946 |
| 1s(2) 4s(1) 5s(1) | -0.00019733 | 0.00000000 |
| 1s(2) 4p(2) | 0.00182955 | 0.00184355 |
| 1s(2) 4p(1) 5p(1) | 0.00032665 | 0.00000000 |
| 1s(2) 4d(2) | -0.00361419 | -0.00363174 |
| 1s(2) 4d(1) 5d(1) | 0.00030308 | 0.00000000 |
| 1s(2) 4f(2) | 0.00618640 | 0.00621375 |
| 1s(2) 4f(1) 5f(1) | -0.00048678 | 0.00000000 |
| 1s(2) 5s(2) | -0.00160546 | -0.00136552 |
| 1s(2) 5p(2) | -0.00141498 | -0.00149216 |
| 1s(2) 5d(2) | -0.00103723 | -0.00101914 |
| 1s(2) 5f(2) | 0.00188266 | 0.00185530 |
| 1s(2) 5g(2) | -0.00284386 | -0.00284386 |

Table 5: Comparison of Be $n = 5$-valence eigenvectors in the MCHF and NO bases.
Table 6: Fine structure total energies of O\(^{+4}\) 1\(s^2\)2\(s\)2\(p\) 3\(P^o\)

| model | energy (a.u.) | energy difference (a.u.) |
|-------|---------------|--------------------------|
| 1\(s^2\)2\(s\)2\(p\) 3\(P^o\) \(^0\) | -68.032 086 | | |
| \(^1\) | -68.031 473 | \(\Delta E_{10} = 0.000 613\) |
| \(^2\) | -68.030 102 | \(\Delta E_{21} = 0.001 370\) |

Figure 1: Flowchart of the Density program
Figure 2: Density of Be $^1S$ ground state for different CAS-MCHF wave functions. Density differences have been scaled by a factor 100.

Figure 3: Comparison of the $1s^22s2p$ $^3P^0$, $^3P^1$ and $^3P^2$ radial density functions of O$^{14}$. Density differences have been scaled by a factor 10 000.
Figure 4: Ground state $S$ and $S^-$ density functions [29]. Density differences have been scaled by a factor 30.