Fully numerical calculations on atoms with fractional occupations.
Range-separated exchange functionals

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A recently developed finite element approach for fully numerical atomic structure calculations [S. Lehtola, Int. J. Quantum Chem. 119, e25945 (2019)] is extended to the description of atoms with spherically symmetric densities via fractionally occupied orbitals. Specialized versions of Hartree–Fock as well as local density and generalized gradient approximation density functionals are developed, allowing extremely rapid calculations at the basis set limit on the ground and low-lying excited states even for heavy atoms.

The implementation of range-separation based on the Yukawa or complementary error function (erfc) kernels is also described, allowing complete basis set benchmarks of modern range-separated hybrid functionals with either integer or fractional occupation numbers. Finally, computation of atomic effective potentials at the local density or generalized gradient approximation levels for the superposition of atomic potentials (SAP) approach [S. Lehtola, J. Chem. Theory Comput. 15, 1593 (2019)] that has been shown to be a simple and efficient way to initialize electronic structure calculations is described.

The present numerical approach is shown to afford beyond microhartree accuracy with a small number of numerical basis functions, and to reproduce literature results for the ground states of atoms and their cations for $1 \leq Z \leq 86$. Our results indicate that the literature values deviate by up to 10 $\mu E_h$ from the complete basis set limit. The numerical scheme for the erfc kernel is shown to work by comparison to results from large Gaussian basis set calculations from the literature. Spin-restricted ground states are reported for Hartree–Fock and Hartree–Fock–Slater calculations with fractional occupations for $1 \leq Z \leq 118$.

I. INTRODUCTION

Atoms are the simplest possible unit in chemistry, which is why electronic structure studies on atoms have a long and venerated history. Thanks to the high amount of symmetry that may be used to reduce the number of degrees of freedom in the atomic problem, fully numerical electronic structure approaches on atoms have been possible for a very long time [1]; for instance, a fully numerical configuration interaction calculation on the oxygen atom was reported by Hartree and coworkers over 80 years ago [2].

As the atomic hamiltonian is spherically symmetric, the exact wave function should be rotationally invariant as well. Although the necessary symmetry requirements can straightforwardly be enforced in wave function approaches, the application of density functional theory (DFT) on atoms is surprisingly tricky. In the usual DFT approach, a single Slater determinant is employed, with all orbitals below the Fermi level being fully occupied. Non-relativistically, all $2l + 1$ atomic orbitals sharing the principal quantum number $n$ and angular quantum number $l$ should be completely degenerate; however, this behavior is broken by conventional DFT as well as Hartree–Fock (HF) already on the first row. Different choices for the occupied orbitals on the $2p$ shell yield different final energies for e.g. B and F, which may lead to several kcal/mol differences in the total energy – with a symmetrized density yielding yet another result [3]. One possibility to obtain comparable results is to employ a standard set of electronic occupations [6], but such an approach does not yield the lowest possible energy.

Pursuing the lowest energy is not unproblematic, either. While HF is infamous for possessing variational solutions that break symmetry in systems with a high degree of symmetry [7], symmetry breaking is a problem in DFT as well [8]. In atoms, broken symmetries often arise for open shells, and the effect of non-spherical densities is known to be more pronounced with functionals at the generalized gradient approximation (GGA) and especially the meta-GGA (mGGA) level than at the local density approximation (LDA) level [9,10]: even optimized effective potential exact-exchange calculations are subject to spurious energy splittings [11]. Inclusion of current density dependence leads to improvement of GGA and mGGA results [12], but the proper orbital degeneracy is still not fully restored.

Symmetry breaking effects in atoms can be seen already at the simplest possible level of DFT, that is, the exchange-only LDA, which is also commonly known as Hartree–Fock–Slater (HFS) theory. For
example, HFS calculations on the F atom reveal mil-
hlihartree decreases of the total energy upon addition
of d as well as f functions, which is at variance to the
generally accepted electronic configuration of fluo-
ris as 1 s^2 2s^2 2p^5. Interestingly, this kind of symme-
try breaking sometimes happens even in the case of
closed-shell atoms; see, for instance, our recent finite
element reproduction [13] of calculations on atomic
anions [15] where symmetry breaking was observed for H^-, Be^-, Li^-, and Na^-.

In addition to being degenerate due to symmetry
(as often in atoms), orbitals may also be degenerate
by accident. Since the aufbau rule implies popula-
ting the orbitals in increasing energy, it tempting to
divide the occupations evenly in the case of degen-
eracies. This paves the way to the use of fractional
occupations, which in the case of atoms naturally
yield a spherically symmetric density thanks to Un-
sold’s theorem [10]; the use of fractional occupations
can be formally justified within the theory of ensem-
ble representable densities [17, 18].

Fractionally occupied orbitals should especially be
used in the case where there is a negative gap be-
tween the highest occupied and lowest unoccupied
orbital no matter which way the orbitals are occu-
pied; this happens when the highest occupied and
lowest unoccupied orbital switch places during the
orbital optimization. In this case, the total energy
can be lowered by moving a fraction of an electron
from the highest occupied orbital to the lowest un-
occupied orbital, and at some point the two levels
should cross.

Fractional occupations have been shown to yield
better results for strongly correlated systems [19–
23]. However, fractional occupations can only be
justified at the Fermi level [24] and more recently it
has been shown that energy minimization naturally
leads to integer occupations below the Fermi level,
and possible fractional occupations at the Fermi
level for independent particle models like HF and
DFT [25].

While in some systems it is clear a priori from
symmetry arguments or the orbital energies how
many orbitals should be fractionally occupied, this
is generally not the case. However, fractional occu-
pations can be obtained as [26] the zero-temperature
limit of finite-temperature DFT (FT-DFT) [27, 28].
In a finite-temperature approach, the fractional or-
bital occupation numbers are determined by the or-
bital energies according to some smearing scheme
that is typically controlled by a single parameter,
an electronic temperature. Because of the simplic-
ity and favorable computational scaling of FT-DFT,
it has become a powerful tool for approximate mod-
ing of systems exhibiting strong correlation; such
approaches have been used to obtain promising re-
sults for a variety of systems [29–43].

Finite electronic temperatures may also be used
to aid the convergence of self-consistent field calcu-
lations of molecules [44]; in the solid state, the use
of fractional occupation numbers is often mandatory
in order to attain convergence [45]. Although finite
temperature approaches are more attractive for DFT
where all electrons experience the same potentials,
fractional temperature approaches can also be used in
the context of HF calculations where they may off-
ger good active spaces for post-HF calculations on
strongly correlated systems [46].

Although several types of smearing schemes have
been suggested, including Fermi-Dirac [27], Gaus-
sian smearing [47], Methfessel–Paxton smearing [48],
cold smearing [49], and others [50], they have been
shown to yield similar results if the parameters are
adjusted properly [46, 51, 52]; however, the behav-
or with respect to temperature needs to be care-
fully checked in each case to ensure convergence
[53]. Note that the evaluation of forces in finite-
temperature calculations require the consideration
of an additional entropic term that arises from the
non-integer occupations and that depends on the
smearing function [54, 55].

Regardless of the used temperature, calculations
with fractional occupations are more involved than
those with integer occupations. Convergence accel-
eration techniques such as direct inversion in the
iterative subspace [56, 57] (DIIS) become invalid
when the orbital occupation pattern changes, even
though the self-consistent field problem itself may
become easier with fractional occupation numbers
[44]. Determining the correct occupations is hard,
since the orbital occupations depend on the orbital
energies, which in turn depend on the orbital occu-
pations. The changes in the occupations may also
cause changes in the shapes of the orbitals, meaning
that the orbitals, their energies and their occupa-
tions need to be solved self-consistently. Several
approaches have been proposed for solving this prob-
lem both for zero [26, 58–60] and finite electronic
temperatures [50, 61, 62].

In systems with a high degree of symmetry such
as atoms, the fractional occupations can be defi-
ded by symmetry block. Fractional occupations
for atoms are typically defined in terms of atomic
shells, over which the electrons are equally divided.
For instance, the 1s^2 2s^2 2p^5 configuration for F im-
plies that the hole in the 2p shell can be equally di-
vied, resulting in the minority spin occupations
2p_x^2/3 2p_y^2/3 2p_z^2/3; a spin-restricted variant would em-
ploy occupations of 2p_x^5/6 2p_y^5/6 2p_z^5/6 in both spin
channels. Indeed, this is the method of choice for
fully numerical density functional calculations on
atoms [1], and it has been used e.g. in ref. [62] for
local density calculations on $1 \leq Z \leq 92$ at the
ground state electronic configuration from experiment, and in ref. [63] for Perdew–Burke–Ernzerhof
(PBE) [68, 69] calculations on $1 \leq Z \leq 20$ and
$31 \leq Z \leq 36$.

Atomic calculations with fractional occupation
numbers are also typically used to generate pseudopotentials [70, 71], numerical atomic orbital basis
functions [72, 73], and Gaussian basis sets [74–76]. Spin-restricted spherically symmetric atoms
may also be used for setting up frozen core calculations within all-electron approaches, and to
determine approximate binding energies [77]. We have
also recently shown that the radial potential from
atomic calculations with fractional occupation numbers can be used to formulate efficient initial guesses
for electronic structure calculations on polyatomic systems via the superposition of atomic potentials
(SAP) approach [78].

In the typical case, electrons are divided evenly
among the $2l+1$ orbitals that are degenerate by
symmetry. However, the fractional occupations can
be generalized beyond integer occupations per shell, in case accidental degeneracy is also present. Early
multiconfigurational HF calculations on atoms found
that the $3d$ orbitals became occupied before the
$4s$ orbitals in transition metals [73, 80], which was
solved by moving fractions of an electron between
the shells. One example of this approach is the iron
atom, where the $[\text{Ar}]3d^{5}4s^{1}$ and $[\text{Ar}]3d^{4}4s^{3}$ configurations both turn out to have a negative gap in
the local-density approximation [81], the upper and
lower indices denoting spin-up and spin-down elec-
trons, respectively. With the Vosko–Wilk–Nusair
(VWN) local density functional, the lowest-energy configuration is found to be $[\text{Ar}]3d^{5}_{1.3984}4s^{1}_{0.602}$ [26].

A systematic, non-relativistic study for spherical
atoms $1 \leq Z \leq 86$ has recently been presented by
Kraisler, Makov and Kelson for the local density and
PBE functionals based on three local density functionals, employing 16 000 point grids and wave functions converged to $2 \mu E_h$ [82]. It was found in ref. [82] that the ground state of most atoms does not in-
volve fractional splitting of electrons between shells, indicating that a fully numerical program for mod-
eling atoms with spherical densities would go a long
way towards the final solution.

While several programs exist for either wave func-
tion or density functional based fully numerical cal-
culations on atoms [11], we are not aware of any pub-
licly available software that supports hybrid functional, except the recently published HELFEM pro-
gram [14, 58], which also includes a fully numerical
approach for diatomic molecules that similarly supports hybrid functionals [54]. Most publicly
available programs for fully numerical density func-
tional calculations on atoms target the generation of projector-augmented wave (PAW) setups [55] or the
generation of pseudopotentials [60]. Although
Hartree–Fock pseudopotential generators have been available for some time [57, 58], which allowed the
use of non-self-consistent pseudopotentials for hy-
brid functionals [59], surprisingly, the self-consistent
generation of pseudopotentials for hybrid function-
als has only been described last year [90], explaining the scarcity of such programs.

Interestingly, the work of Yang et al in ref. [90] did not employ fractionally occupied Hartree–Fock cal-
culations, but rather followed Slater’s multiconfigu-
rational approach, which is at odds with the density
functional description used in the work, as the ex-
act exchange and density functional parts experience
different electron densities. In contrast, when frac-
tional occupations are employed as in the present
work, the exchange exact operator becomes indepen-
dent of the magnetic quantum number $m$ as will be
shown in section 11.3 and both the density func-
tional and exact exchange operators are evaluated
with the same density matrix.

Although a general-use atomic program like the
one in HELFEM can be straightforwardly adapted
to calculations on spherically symmetric densities by
employing fractional occupation numbers in the con-
struction of the density matrix, a more efficient ap-
proach is afforded by taking the assumption of the
spherical symmetry of the density matrix deeper in
the algorithms. As a result, some or even all of the
angular integrals can be eliminated from the calcula-
tions, reducing the problem to a small number of di-
ensions; indeed, this is exactly what is done in the
multiconfigurational HF approach Slater proposed 90 years ago [91].

In the present work, we describe the extension of
the atomic program in HELFEM to the descrip-
tion of atoms with spherical symmetric density via
fractional occupation numbers. Unlike the other
programs in HELFEM, the spherically symmetric
atomic program is interfaced to the LIBXC library
of density functionals [92] and can be used with all
supported density functionals therein. Specialized
implementations for atomic calculations with frac-
tional occupations are developed for local density
(LDA) and generalized gradient (GGA) functionals
as well as HF exchange, yielding significant reduc-
tions in the dimensionality of the problem, whereas
meta-GGA functionals can be used via an interface
to the algorithms previously developed in ref. [14].

Importantly, we also describe the implementa-
tion of Yukawa and complementary error function
(eric) range-separated exchange for atomic calcula-
tions in HELFEM with either fractional or integer
occupations, allowing complete basis set benchmarks
of recently developed exchange-correlation functionals such as the CAM-QTP family by Bartlett and coworkers \cite{93, 94}, the N12-SX and revM11 functionals by Truhlar and coworkers \cite{96, 97}, and the \omega B97X-V and \omega B97M-V functionals by Mardirossian and Head-Gordon (without the non-local correlation part) \cite{98, 99}. While the spherical harmonics decomposition for the Yukawa kernel is well known, the decomposition for the erfc kernel has only been derived some time ago \cite{100} and does not appear to have been implemented within a generally applicable fully numerical approach for atoms. Results for H and He with relatively low-order B-spline basis sets have, however, been published almost simultaneously to our work \cite{101}. Finally, we also describe the analytic calculation of the radial potentials necessary for the SAP orbital guess \cite{75}.

In the next section, we derive the equations for fractionally occupied HF and DFT at the LDA and GGA levels of theory. Then, in the Results section, we present applications of the program to reproducing ground states for the neutral atoms and cations 1 \leq Z \leq 86 and compare with ref. 82; we reproduce the long-range corrected density functional calculations on closed-shell atoms of ref. 13 to show that the range-separation scheme works; and finally we report the range corrected density functional calculations on and compare with ref. 82; we reproduce the long-range exact exchange.

### II. METHOD

A basis set of the form

\[ \chi_{nlm} = r^{-1}B_n(r)Y_l^m(\theta, \phi) \]  

is adopted as in the integer-occupation program described in ref. 14. Here, \( B_n(r) \) are the piecewise polynomial shape functions of the finite element method, which have been discussed extensively in refs. \cite{102, 103} to which we refer for further details.

#### A. Range-separated exchange

As discussed in refs. \cite{1, 14}, the key to fully numerical electronic structure calculations on atoms is the Laplace expansion

\[ \frac{1}{r_{12}} = \sum_{L=0}^{\infty} \frac{4\pi}{2L+1} \frac{1}{r_>} \left( \frac{r_<}{r_>} \right)^L \sum_{M=-L}^{L} Y_L^M(\Omega_1) \left( Y_L^M(\Omega_2) \right)^* \]  

that factorizes the two-electron integrals

\[ \langle ij|kl \rangle = \int \frac{\chi_i(r)\chi_j^*(r)\chi_k(r')\chi_l^*(r')}{|r-r'|} d^3r d^3r' \]  

into a radial and an angular part.

In range-separated density functional theory \cite{102, 103}, the Coulomb interaction is split into a short-range (sr) and a long-range (lr) part as

\[
\frac{1}{r} = \frac{\phi_{sr}(r)}{r} + \frac{1 - \phi_{sr}(r)}{r} = \frac{\phi_{lr}(r)}{r} + \frac{\phi_{lr}(r)}{r},
\]

where \( \phi_{sr}(r) = 1 - \phi_{lr}(r) \) is a splitting function. Typically, the short-range part is described using density functional theory, and the long-range part with HF theory, but in practice many functionals employ more flexibility: for instance, the CAM-B3LYP functional \cite{104} contains 19% short-range and 65% long-range exact exchange.

The evaluation of the range-separated exchange functionals is simple if one has access to the Green’s function expansion of the range-separated kernel as

\[
\frac{\phi_{sr}(r)}{r_{12}} = \sum_{L=0}^{\infty} \frac{4\pi}{2L+1} G_L(r_<, r_>, \mu) \times \sum_{M=-L}^{L} \left( Y_L^M(\Omega_1) \right)^* Y_L^M(\Omega_2)
\]

where \( G_L(r_<, r_>, \mu) \) is the Green’s function, \( r_> \) and \( r_< \) are the greater and smaller of \( r_1 \) and \( r_2 \), respectively, and \( \mu \) is the range separation parameter.
The Green’s function for the (unscreened) classical Coulomb interaction can be identified from equation (2) as

$$G_L^\text{Coulomb}(r_>, r_<) = \frac{r_{L}^2}{r_{L+1}}.$$  \hspace{1cm} (6)

The implementation of the integrals in HELFEM is based on the primitive integrals defined in ref. 14 as

$$I_{ijkl}^L = \frac{4\pi}{2L + 1} \int dr_1 dr_2 B_i(r_1) B_j(r_2) \times B_k(r_2) B_l(r_2) G_L(r_>, r_<, \mu, \nu), \hspace{1cm} (7)$$

where $B_i(r)$ are the piecewise polynomial basis functions of equation (11).

1. Yukawa kernel

The Yukawa-screened potential, $\phi_r(r_{12}) = \exp(-\lambda r_{12})$ has a relatively well-known simple expansion

$$\frac{e^{-\lambda |r-r'|}}{|r-r'|} = 4\pi \lambda \sum_{L=0}^{\infty} i_L(\lambda r_<) k_L(\lambda r_>) \times \sum_{M=-L}^{L} Y_L^M(\Omega_1) \left(Y_L^M(\Omega_2)\right)^* \hspace{1cm} (8)$$

where $i_L$ and $k_L$ are regular and irregular modified Bessel functions that are regular at zero and infinity, respectively. Due to its separability, Yukawa-screened functionals are easy to handle in fully numerical approaches. Indeed, the Yukawa Green’s function is employed in several recently developed linear scaling approaches for solving the HF or Kohn–Sham equations for bound orbitals in molecular systems via the Helmholtz kernel [106–110]. The Yukawa interaction is also straightforward to implement in calculations with Slater-type orbitals [111–113]. It turns out that Yukawa screening can also be implemented with Gaussian-type orbitals in a rather straightforward manner [114], as analogous integrals also arise within $r_{12}$ wave function theory [115–116]. Such implementations are, however, rare at the moment, even though it has been claimed that Yukawa screening yields more accurate atomization and charge transfer excitation energies than erfc screening [117]. The Green’s function for the Yukawa interaction can be read from equation (8) as

$$G_L^\text{Yukawa}(r_>, r_<, \lambda) = (2L + 1) \lambda i_L(\lambda r_<) k_L(\lambda r_>).$$  \hspace{1cm} (9)

As the Yukawa interaction factorizes in $r_>$ and $r_<$, it can be implemented in a similar fashion to the full Coulomb interaction, equation (6), along the lines of ref. 14.

2. erfc kernel

Most range-separated functionals, however, are based on the complementary error function (erfc) kernel $\phi_{\text{erfc}}(r) = \text{erfc}(\mu r)$. Such functionals are easy to implement in Gaussian-basis programs, requiring but simple modifications to the two-electron integrals [118–119], as well as plane wave programs since the kernel has a simple Fourier transform which is strongly attenuated at large momentum. In contrast, the implementation of the erfc kernel is more complicated in real-space approaches. Fortunately, spherical harmonic expansions for the erfc Green’s functions are available in the literature [100, 120], but their form is more involved than that of the Yukawa function in equation (8). The main complication is that the Green’s function does not factorize in $r_<$ and $r_>$, which means that two-dimensional quadrature is always required. In the approach of ref. 100, new variables are introduced as $\Xi = \mu R$ and $\xi = \mu r$ and

$$G_L(R, r; \mu) = \mu \Phi_L(\Xi, \xi) \hspace{1cm} (10)$$

where $\Phi_L$ is a scaled radial function given by

$$\Phi_n(\Xi, \xi) = F_n(\Xi, \xi) + \sum_{m=1}^{n} F_{n-m}(\Xi, \xi) \frac{\xi^{2m} + \xi^{2m}}{\Xi^{m}} H_n(\Xi, \xi) \hspace{1cm} (11)$$

$$F_n(\Xi, \xi) = \frac{2}{\sqrt{\pi}} \sum_{p=0}^{n} \left(-\frac{1}{4 \Xi \xi}\right)^{p+1} \frac{(n+p)!}{p!(n-p)!} \left((-1)^{n-p} e^{-(\xi+\Xi)2} - e^{-(\xi-\Xi)^2}\right) \hspace{1cm} (12)$$

$$H_n(\Xi, \xi) = \frac{1}{2(\Xi^2 + \xi^2)^{n+1}} \left[(\Xi^{2n+1} + \xi^{2n+1}) \text{erfc}(\Xi + \xi) - (\Xi^{2n+1} - \xi^{2n+1}) \text{erfc}(\Xi - \xi)\right] \hspace{1cm} (13)$$

(Note that the lower limit of the sum in equation (12) is incorrect in ref. 100, where it reads $p = 1$ instead
of $p = 0$.) Equations (11) to (13) are numerically unstable in the short range, which is why when either

$$\xi < 0.4,$$

or $\Xi < 0.5$ and $0 < \xi < 2\Xi$, the Green’s function is evaluated with a Taylor expansion

$$\Phi_n(\Xi, \xi) = \sum_k D_{n,k}(\Xi) \xi^{n+2k},$$

(14)

$$D_{n,0}(\Xi) = \text{erf} \Xi + \frac{\exp(-\Xi^2)}{\sqrt{\pi}} (2\Xi^2)^{n+1} \sum_{m=1}^{n} \frac{(2\Xi^2)^{-m}}{(2n - 2m - 1)!!}$$

(15)

$$D_{n,k}(\Xi) = \frac{\exp(-\Xi^2)}{\sqrt{\pi}} (2\Xi^2)^{n+1} \sum_{m=1}^{2n + 1} \frac{2n + 1}{k!(2n + 2k + 1)} \left( \frac{m - k - 1}{m - 1} \right) \frac{(2\Xi^2)^{k-m}}{(2n + 2k - 2m - 1)!!}, \quad k \geq 0$$

(16)

Despite the lack of factorization of the erf $\text{c}$ Green’s function, its evaluation can be carried out analogously to the Coulomb and Yukawa kernels. The primitive integrals, equation (7), can be divided into two cases thanks to the finite support of the piecewise polynomial basis functions, as discussed in ref. [14]. In an intraelement integral, both $ij$ and $kl$ are within the same element, whereas in an interelement integral $ij$ are in one element and $kl$ are in another. In analogy to the scheme for Coulomb integrals discussed in ref. [14], the interelement integrals are evaluated with $N_{\text{quad}}$ quadrature points in both $ij$ and $kl$, whereas the intraelement integrals employ $N_{\text{quad}}$ points in $ij$, whereas the $kl$ quadrature is split into $N_{\text{quad}}$ intervals, all of which employ a fresh set of $N_{\text{quad}}$ quadrature points.

B. Self-consistent field calculations with fractional occupations

It is well known that atomic orbitals can be written in the form

$$\psi_{nlm}(r) = R_{nl}(r)Y_{l}^{m}(\hat{r}).$$

(17)

Employing smeared occupations as

$$n(r) = \sum_{n=1}^{\infty} \sum_{l=-n}^{n} f_{nl} |\psi_{nlm}(r)|^2$$

(18)

$$= \sum_{nl} f_{nl} (2l + 1) R_{nl}^2(r) \frac{4\pi}{4\pi} = n(r)$$

(19)

where $f_{nl}$ is the occupation number of all the $2l + 1$ orbitals on the $(n,l)$ shell, one immediately sees that the density matrix is diagonal in $l$ and $m$

$$P^\sigma_{\mu\nu} = \delta_{\mu l} \delta_{\nu m} \delta_{m^\prime} \delta_{l^\prime} \left[ \phi_{\mu}(r) \phi_{\nu}(r) \right]$$

(20)

and that the elements of the density matrix only depend on the value of $l$. The spherical averaging yields huge simplifications for density functional calculations. As now the density is only a function of the radial coordinate, also its gradient

$$\nabla n = \partial_r n \hat{e}_r$$

(21)

only depends on the radial coordinate. Following the usual projective approach [14,121], the LDA and GGA matrix elements

$$K^{\sigma \tau}_{\mu \nu} = \int \left[ \frac{\delta f_{\sigma c}}{\delta n_{\sigma}(r)} \phi_{\mu}(r) \phi_{\nu}(r) + 2 \frac{\delta f_{\sigma c}}{\delta \gamma_{\sigma \tau}(r)} \nabla \rho_{\sigma}(r) + \frac{\delta f_{\sigma c}}{\delta \gamma_{\sigma \tau}(r)} \nabla \rho_{\sigma^\prime}(r) \right] \cdot \nabla \left[ \phi_{\mu}(r) \phi_{\nu}(r) \right] d^3r$$

(22)

become greatly simplified as only the radial terms are picked up, and as the same radial basis is used for all $l, m$; see equation (14). Note, however, that meta-GGAs that depend on the kinetic energy density cannot be handled in the same fashion, as the kinetic energy density is not manifestly dependent only on the radial coordinate as discussed e.g. in ref. [122]. Alike the exact exchange discussed below, the meta-GGA potential turns out to depend on the $l$ channel. Meta-GGA functionals can be used in
the present program via a fractional-occupation interface to the full atomic routines discussed in ref. 14.

The Coulomb matrix arising from equation (2) trivially reduces to a single term as the spherically symmetric density only consists of a single \( L = 0 \), \( M = 0 \) component. Exact exchange – either with the full Coulomb form of equation (6) or the range-separated versions in equations (9) and (10) – is a bit more complicated, as both the integrals and the density matrix carry a dependence on the orbital angular momenta in the well-known equation

\[
K_{\mu\nu} = \sum_{\sigma\tau} (\mu\sigma|\nu\tau) P_{\sigma\tau}.
\]

Employing the blocking of the density matrix given in equation (20), the exchange matrix can be written as

\[
K_{\mu\nu}^{\text{out}} = \sum_{\sigma\tau} (\mu\sigma|\nu\tau) P_{\sigma\tau} = \sum_{L = |l_{\text{in}} - l_{\text{out}}|}^{l_{\text{in}} + l_{\text{out}}} \frac{P_{\mu\nu \sigma\tau} L_{\mu\nu \sigma\tau}^{\text{out}} P_{\sigma\tau}^{\text{in}}}{2l_{\text{out}} + 1} \sum_{m_{\text{in}} = -l_{\text{in}}}^{l_{\text{in}}} \sum_{m_{\text{out}} = -l_{\text{out}}}^{l_{\text{out}}} G_{L_{\text{in}} m_{\text{in}}, l_{\text{out}} m_{\text{out}}} M_{m_{\text{in}}, l_{\text{out}}} M_{m_{\text{out}}, l_{\text{out}}} (24)
\]

where \( L \) is a coupled angular momentum with \( z \) projection \( M = m_{\text{out}} - m_{\text{in}} \). Rearranging the contractions, it is then seen that

\[
K_{\mu\nu}^{\text{out}} = \sum_{L} \frac{P_{\mu\nu \sigma\tau} L_{\mu\nu \sigma\tau}^{\text{out}} P_{\sigma\tau}^{\text{in}}}{2l_{\text{out}} + 1} \sum_{m_{\text{in}} = -l_{\text{in}}}^{l_{\text{in}}} \sum_{m_{\text{out}} = -l_{\text{out}}}^{l_{\text{out}}} G_{L_{\text{in}} m_{\text{in}}, l_{\text{out}} m_{\text{out}}} M_{m_{\text{in}}, l_{\text{out}}} M_{m_{\text{out}}, l_{\text{out}}} (25)
\]

where the evaluation is done from the insidemost bracket out.

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C. Cusp condition

One way to diagnose atomic wave functions is the Kato–Steiner cusp condition [123, 124]

\[
C = -\frac{1}{2Z} \frac{d \log n(r)}{dr} \bigg|_{r=0} = -\frac{1}{2Z} \frac{n'(0)}{n(0)} (26)
\]

which yields the value \( C = 1 \) for the exact HF or density functional solution [125]. The electron density \( n(r) \) at the nucleus was obtained in ref. 14 via l'Hôpital’s rule as

\[
n(0) = P_{\mu\nu} \lim_{r \to 0} \frac{B_{\mu}(r)B_{\nu}(r)}{y^2} (27)
\]

\[
= P_{\mu\nu} \lim_{r \to 0} \frac{\frac{d^2}{dr^2}B_{\mu}(r)B_{\nu}(r)}{y^2} (28)
\]

\[
= P_{\mu\nu} B_{\mu}'(r)B_{\nu}'(r). (29)
\]

Its derivative at the nucleus also turns out to have a simple expression:

\[
n'(0) = P_{\mu\nu} \lim_{r \to 0} \left[ \frac{B_{\mu}'(r)B_{\nu}(r)}{y^2} + \frac{B_{\mu}(r)B_{\nu}'(r)}{y^2} - 2 \frac{B_{\mu}(r)B_{\nu}(r)}{r^3} \right]
\]

\[
= P_{\mu\nu} \lim_{r \to 0} \left[ \frac{\frac{d^3}{dr^3}B_{\mu}(r)B_{\nu}(r)}{y^2} - \frac{2}{y^2} \frac{\frac{d}{dr}B_{\mu}(r)B_{\nu}(r)}{r^2} \right] = P_{\mu\nu} B_{\mu}''(0)B_{\nu}'(0). (30)
\]

The value of the cusp is printed out at the end of all atomic calculations in HELFEM.
D. Effective radial potential for SAP

In the SAP approach discussed in ref. 78, approximate orbitals for a molecule are obtained by diagonalizing an effective one-body Hamiltonian in an external potential obtained as a superposition of radial atomic potentials. Once the atomic ground state has been found with any supported method in HELFEM, including HF and hybrid and meta-GGA functionals, the radial effective potential for the SAP approach can be calculated based on any LDA or GGA functional. Extensions to the exact exchange, as in the optimized effective potential method [126], as well as generalized Kohn–Sham methods for the radial potentials from meta-GGA functionals are left for future work.

If the radial potential is self-consistent, i.e. the same functional was used for both the atomic orbitals and the potential, the SAP guess will reproduce the atomic orbitals exactly [78]. The atomic potential comprises Coulomb and exchange-correlation contributions, the calculation of which is presented in the following.

1. Coulomb potential

Employing the Laplace expansion, equation (2), the Coulomb potential at a point \( r \) for a spherically symmetric charge distribution is

\[
V(r) = \int_0^\infty \frac{1}{r'} n(r') r^2 \, dr'
\]

(31)

Expressing the orbitals as in equation (17) yields potential matrix elements of the form

\[
V_{ij}(r) = \int_0^\infty \frac{1}{r'} B_i(r') B_j(r') \, dr'
\]

(32)

\[
= \frac{1}{r} \left[ \int_0^r B_i(r') B_j(r') \, dr' + \int_r^\infty \frac{1}{r'} B_i(r') B_j(r') \, dr' \right]
\]

(33)

and one gets three cases depending on whether \( r \) is inside the element where \( i \) and \( j \) reside, or not. Let the element begin at \( r_b \) and end at \( r_e \). Now

Like the two-electron integrals discussed above, the in-element potential \( r_b < r < r_e \) has to be evaluated by slices at every radial quadrature point \((r_0, r_1, \ldots, r_{n-1})\)

\[
\begin{align*}
\int_{r_b}^{r_{k-1}} B_i(r') B_j(r') \, dr' &= \int_{r_b}^{r_0} B_i(r') B_j(r') \, dr' + \sum_{l=1}^{k-1} \int_{r_{l-1}}^{r_l} B_i(r') B_j(r') \, dr' \\
\int_{r}^{r_{e-1}} B_i(r') B_j(r') \, dr' &= \int_{r_{n-1}}^{r_e} r'^{-1} B_i(r') B_j(r') \, dr' + \sum_{l=k}^{n-1} \int_{r_{l-1}}^{r_l} r'^{-1} B_i(r') B_j(r') \, dr'
\end{align*}
\]

(35)

(36)

2. Exchange-correlation potential

The functional derivative satisfies

\[
\delta E = E[n + \delta n] - E[n] = \int \frac{\delta E}{\delta n} \delta n \, d^3r.
\]

(37)

and so

\[
\delta E = \int \left( \frac{\delta E}{\delta n} \delta n + \frac{\delta E}{\delta \nabla n} \delta \nabla n \right) \, d^3r.
\]

(38)

Integrating by parts one gets

\[
\delta E = \int \nabla \frac{\delta E}{\delta \nabla n} \delta \nabla n \, d^3r
\]

(39)

\[
= - \int \nabla \frac{\delta E}{\delta \nabla n} \delta \nabla n \, d^3r
\]

(40)
from which one can identify

\[ v(r) = \delta E_{\delta n} - \nabla \delta E_{\delta n}. \quad (41) \]

Expressing the functional in terms of

\[ \gamma^{\sigma\sigma'} = \nabla n^\sigma \cdot \nabla n^{\sigma'} \quad (42) \]

one has

\[ \frac{\delta}{\delta \nabla n} \delta n = \frac{\delta \gamma}{\delta \nabla n} \frac{\delta}{\delta n} = 2 \nabla n \quad (43) \]

and so

\[ v(r) = \frac{\delta E}{\delta n} - 2 \nabla \left( \frac{\delta E}{\delta \gamma} \nabla n \right) \quad (44) \]

or for an open shell system

\[ v^\sigma(r) = \frac{\delta E}{\delta n^\sigma} \nabla \left( 2 \frac{\delta E}{\delta \gamma^{\sigma\sigma'}} \nabla n^\sigma + \frac{\delta E}{\delta \gamma^{\sigma\sigma'}} \nabla n^{\sigma'} \right) \quad (45) \]

where \( \sigma \neq \sigma' \).

To guarantee accuracy, the gradient terms have to be evaluated analytically. Fortunately, there’s only radial dependence, so the gradient

\[ \nabla f = \left( \frac{\partial f}{\partial r}, 0, 0 \right) \quad (46) \]

can be replaced by a radial derivative, and the divergence with

\[ \nabla \cdot A = \left( \frac{1}{r^2} \frac{\partial}{\partial r} \left( r^2 A_r \right), 0, 0 \right) = \left( \frac{\partial}{\partial r} A_r + \frac{2 A_r}{r}, 0, 0 \right) \quad (47) \]

Now,

\[ \partial_r \left( \frac{\delta E}{\delta \gamma^{\sigma\sigma'}} \partial_r n^{\sigma'} \right) = \left( \frac{\partial}{\partial r} \frac{\delta E}{\delta \gamma^{\sigma\sigma'}} \right) \partial_r n^{\sigma'} + \frac{\delta E}{\delta \gamma^{\sigma\sigma'}} \partial_r^2 n^{\sigma'} \quad (48) \]

where

\[ \partial_r \left( \frac{\delta E}{\delta \gamma^{\sigma\sigma'}} \partial_r n^{\sigma'} \right) = \frac{\partial n^\tau}{\partial r} \left( \frac{\partial}{\partial n^\tau} \frac{\delta E}{\delta \gamma^{\sigma\sigma'}} \right) + \frac{\partial \gamma^{\tau\tau'}^\sigma}{\partial \gamma^{\tau\tau'}^\sigma} \frac{\delta E}{\delta \gamma^{\sigma\sigma'}} \quad (49) \]

where we have defined \( g^\sigma = \partial_r n^\tau \) and \( l^\tau = \partial_r^2 n^\tau \), and the extra \( 2 A_r / r \) term from the divergence, equation (47), yielding

\[ \frac{2}{r} \left( 2 \frac{\delta E}{\delta \gamma^{\sigma\sigma'}} g^\sigma + \frac{\delta E}{\delta \gamma^{\sigma\sigma'}} g^{\sigma'} \right). \quad (50) \]

Thus, altogether, the radial exchange(-correlation) potential is given by

\[ v^\sigma_{xc}(r) = \frac{\delta E}{\delta n^\sigma} - \nabla \cdot \left( 2 \frac{\delta E}{\delta \gamma^{\sigma\sigma'}} \nabla n^\sigma + \frac{\delta E}{\delta \gamma^{\sigma\sigma'}} \nabla n^{\sigma'} \right) \quad (51) \]

where the various derivatives of the exchange-correlation functional are available in LIBXC [92].

### III. RESULTS

To demonstrate the new routines, we reproduce literature values for the ground states of the neutral
and cationic atoms $1 \leq Z \leq 86$ with the VWN functional, as well as a Perdew–Burke–Ernzerhof (PBE) \cite{Perdew96, Perdew97} functional based on VWN correlation \cite{Perdew96}, accurate values for which were obtained in ref. \cite{Perdew96} with 10,000 radial grid points. We found that by using a radial basis consisting of ten 15-node elements and a practical infinity $r_{\infty} = 40a_0$, the energy has converged beyond microhartree accuracy, even though this basis contains just 139 radial basis functions – almost two orders of magnitude fewer degrees of freedom than used in ref. \cite{Perdew96}. These results, with differences to the reference data from ref. \cite{Perdew96} are shown in table I for neutral atoms and table II for their cations.

The agreement to most part is excellent: large positive differences that indicate the value of ref. \cite{Perdew96} is lower are seen for the species for which the calculations in ref. \cite{Perdew96} transferred fractional charge across shells. Otherwise, the differences become noticeable for heavier atoms, nearing $-10 \mu E_h$ when $Z \to 86$, indicating that the data in ref. \cite{Perdew96} is not fully converged to the basis set limit. In our VWN calculation on the La$^+$ cation, it was discovered that the energy for the 4$f^8$ state reported in ref. \cite{Perdew96} was incorrect; the correct energy is $-8217.456974$ \cite{Erkale19}. Next, we demonstrate that the erf range-separation scheme works by reproducing literature values for the total energies of the spherically symmetric atoms on the first two rows using the long-range corrected BLYP functional \cite{Clementi90, Erkale15, Erkale16}. In ref. \cite{Erkale15} we investigated the accuracy of the aug-pc-$\infty$ Gaussian basis set that was used in ref. \cite{Erkale15}. The study was restricted to $^1S$ states to avoid symmetry breaking effects, which were still observed for H$^-$, He$^-$, Li$^-$, and Na$^-$, as was discussed in the Introduction. Reproducing symmetry preserving data with Erkale \cite{Erkale15}, we found that the truncation error of the aug-pc-$\infty$ basis set is less than 1 $\mu E_h$ for light atoms and tens of $\mu E_h$ for heavier atoms in Hartree–Fock and BHLYP \cite{Erkale16} calculations.

Because the screening is evaluated analytically in Gaussian-basis calculations \cite{Clementi90} and the accuracy of the aug-pc-$\infty$ basis set has been established \cite{Erkale15}, the values reported in ref. \cite{Erkale15} offer an ideal reference for the present work. The comparison of results obtained in the present work with equations \cite{Clementi90} to \cite{Clementi90} and a numerical basis set with five 15-node radial elements and a practical infinity $r_{\infty} = 40a_0$ is shown in table III, demonstrating excellent agreement between the fully numerical and Gaussian basis calculations. The values are in full agreement after rounding to the same accuracy for the light atoms, while the fully numerical values are slightly below the Gaussian-basis values for the heavier atoms, as expected based on the basis set truncation errors observed in ref. \cite{Erkale15}.

Finally, the spin-restricted ground states for all atoms in the periodic table at HF and HFS levels of theory are shown in tables IV and V respectively; these calculations also used ten 15-node radial elements. The data reveal that in some cases a lower-lying configuration has been seen in the brute force search, but that it failed to converge. In the HF calculations, the $6s^24f^25d^1$ state of Pr converges without problems; however, the $6s^24f^3$ configuration has a lower energy but its wave function failed to converge. Similar issues are observed in the HFS calculations for Cf, Es, and Fm, where the $5f^{n-1}7s^1$ state converges without problems, but a lower energy is observed for a $5f^n$ configuration the wave function of which fails to converge.

The HF results can be compared to the high-accuracy data for multiconfigurational HF of Saito \cite{Saito87}. Because the present calculations are spin-restricted with fractional occupations, the energies are higher than those reported in ref. \cite{Saito87}. However, the agreement for the noble gases is perfect, underlining the high accuracy of the computational approach used in the present work, which was outlined in ref. \cite{Erkale15}, even though only 139 radial basis functions were employed.

**IV. SUMMARY AND DISCUSSION**

We have described new efficient implementations of range-separated functionals as well as fractional occupations for atomic electronic structure calculations with HelFEM, and demonstrated that beyond microhartree accuracy can be achieved with just 139 numerical radial basis functions. We have tested the program by reproducing local density approximation (LDA) and generalized gradient approximation (GGA) total energies for $1 \leq Z \leq 86$ at the basis set limit, and shown that the literature values deviate from the complete basis set limit by up to 10 $\mu E_h$. The approaches developed in the present work could be straightforwardly extended to fractional occupations per shell in future work, requiring the addition of a logic to formulate the fractional occupation numbers.

The capabilities added to HelFEM in the present work allow for self-consistent benchmarking of density functionals at the basis set limit, which is useful for development and implementation purposes. For instance, Clementi–Roetti wave functions \cite{Clementi90} are often used for non-self-consistent benchmarks of density functionals, but the availability of a program for self-consistent calculations is certain to help future developments as numerical instabilities in the functional may not be detected in non-self-consistent
Table I: Total energies of neutral atoms for calculations with the VWN functional and a PBE functional based on VWN correlation. The differences $\Delta E = E(\text{present work}) - E(\text{Kraisler 2010})$ are calculated relative to the fully numerical values from ref. 82 and are reported in microhartree.

| $Z$ | $E(\text{VWN})$ | $\Delta E(\text{VWN})$ | $E(\text{PBE})$ | $\Delta E(\text{PBE})$ |
|-----|----------------|------------------------|----------------|------------------------|
| 1   | -0.478671      | 0                      | -0.009963      | -0.478671              |
| 2   | -2.834836      | 0                      | -2.893287      | -0.058451              |
| 3   | -7.34957       | 0                      | -7.462726      | -0.013158              |
| 4   | -14.447209     | 0                      | -14.630525     | -0.183326              |
| 5   | -24.353614     | 0                      | -24.606283     | -0.252669              |
| 6   | -37.470031     | 0                      | -37.795116     | -0.325085              |
| 7   | -54.136799     | 0                      | -54.537743     | -0.400944              |
| 8   | -74.527410     | 0                      | -75.003219     | -0.475809              |
| 9   | -109.114192    | 0                      | -109.668342    | -0.554150              |
| 10  | -128.233481    | 0                      | -128.869661    | -0.636180              |
| 11  | -161.447625    | 0                      | -162.176267    | -0.730642              |
| 12  | -199.139406    | 0                      | -200.050461    | -0.911055              |
| 13  | -241.321156    | 0                      | -242.236535    | -0.915379              |
| 14  | -288.222945    | 0                      | -289.236535    | -1.013600              |
| 15  | -340.005794    | 0                      | -341.120757    | -1.114963              |
| 16  | -396.743948    | 0                      | -397.951200    | -1.207252              |
| 17  | -458.671463    | 0                      | -459.790708    | -1.119245              |
| 18  | -525.946195    | 0                      | -527.352025    | -1.405830              |
| 19  | -598.26032     | 0                      | -600.153693    | -1.893370              |
| 20  | -675.742283    | 0                      | -679.167200    | -3.424922              |
| 21  | -758.685248    | 0                      | -760.397795    | -1.712547              |
| 22  | -847.314092    | 0                      | -849.129808    | -1.815716              |
| 23  | -941.786662    | 0                      | -943.704413    | -1.917751              |
| 24  | -1042.218348   | 0                      | -1044.239902   | -2.021554              |
| 25  | -1148.64093    | 0                      | -1150.765145   | -2.124218              |
| 26  | -1261.23291    | 0                      | -1263.441835   | -2.239924              |
| 27  | -1380.193787   | 0                      | -1382.508399   | -2.354612              |
| 28  | -1505.672905   | 0                      | -1508.087914   | -2.465009              |
| 29  | -1637.793358   | 0                      | -1640.102799   | -2.577441              |
| 30  | -1776.573850   | 0                      | -1779.994579   | -3.420730              |
| 31  | -1921.851924   | 0                      | -1924.582672   | -3.730748              |
| 32  | -2073.829860   | 0                      | -2076.672928   | -3.843068              |
| 33  | -2232.587154   | 0                      | -2235.545023   | -3.957869              |
| 34  | -2398.134930   | 0                      | -2401.196896   | -4.012966              |
| 35  | -2570.626651   | 0                      | -2574.240691   | -4.124040              |
| 36  | -2750.147940   | 0                      | -2753.482672   | -4.254732              |
| 37  | -2936.342160   | 0                      | -2939.739646   | -4.404486              |
| 38  | -3129.453161   | 0                      | -3132.963153   | -4.510002              |
| 39  | -3329.525142   | 0                      | -3333.148098   | -4.605946              |
| 40  | -3536.771077   | 0                      | -3540.519040   | -4.738963              |
| 41  | -3751.29618    | 0                      | -3755.160742   | -4.885560              |
| 42  | -3973.162595   | 0                      | -3977.149787   | -5.032202              |
| 43  | -4202.348034   | 1                      | -4206.446961   | -5.098927              |
Table II: Total energies of atomic cations for calculations with the VWN functional and a PBE functional based on VWN correlation. The differences $\Delta E = E_{\text{present work}} - E_{\text{Kraisler 2010}}$ are calculated relative to the fully numerical values from ref. 82 and are reported in microhartree. *An incorrect value was reported in ref. 82 for La$^+$. See main text.
| atom | finite element Gaussian basis |
| --- | --- |
| H  | -0.519949 -0.51995 |
| He | -2.866811 -2.86681 |
| Li | -7.435511 -7.43551 |
| Be | -14.584723 -14.58472 |
| N  | -54.482222 -54.48222 |
| F  | -99.766050 -99.76604 |
| Ne | -128.816627 -128.81661 |
| Na | -162.136564 -162.13655 |
| Mg | -199.907036 -199.90702 |
| P  | -341.069932 -341.06992 |
| Cl | -460.080588 -460.08057 |
| Ar | -527.321257 -527.32124 |

Table III: Comparison of the total energies of spherically symmetric atoms with the LC-BLYP functional with the range separation constant $\omega = 0.3$ reproduced with finite element calculations (present work) and a Gaussian basis set calculation [15].

Furthermore, we have reported the non-relativistic spin-restricted ground state configurations of all atoms in the periodic table at HF and HFS levels of theory. Such knowledge is useful for implementations of the superposition of atomic densities guess [134, 135], which is often implemented based on spin-restricted fractionally occupied calculations. The present approach is also useful for implementations of the SAP guess [78]. For instance, the implementation of SAP now available in the development version of the Psi4 program [136] is based on HFS potentials tabulated during the present work. Instead of the 4000 point tabulation used in ref. [78] with unknown error, the ten-element calculations of the present work yield 751-point tabulations that reproduce the sub-microhartree-level accuracy of the original calculation.

The atomic orbitals obtained from the present approach may also be useful for initializing fully numerical molecular electronic structure calculations via either a superposition of atomic densities, or in combination to the extended Hückel rule developed in ref. [78].

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Table IV: Non-relativistic spin-restricted spherical HF configurations for all elements in the periodic table.

Entries in italic indicate a lower-lying configuration was identified but it failed to converge.

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Entries in italic indicate a lower-lying configuration was identified but it failed to converge.

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