

# Numerical analysis of $N$ -electron atomic statefunctions using local basis sets

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*Abstract:* This contribution presents the numerical analysis of Hartree-Fock's method of computing electron atomic statefunctions using Galerkin's finite element method. The underlying theory and computational implementation are presented in some detail for the first time and highly accurate energies are presented for free neutral atoms, ions, and for the spatially confined He atom. The method of using local basis sets is shown to be competitive with global basis sets of the Slater and modified Slater types in terms of accuracy and use.

*Key-Words:* Atomic physics, Finite element method, Numerical analysis, Quantum confinement

## 1 Introduction

Many-electron atomic statefunctions are often required for the computation of various physical processes involving electron motion and interaction. The champion of numerical methods are those that determine the electron statefunctions in a self-consistent manner and according to a variational principle. For many practical purposes, HF statefunctions are sufficiently accurate and can serve as the basis for more involved computations including strongly correlated electrons.

In general, algebraic approximations to HF statefunctions are expanded as a linear combination of radial orbitals that form the basis for practical computations. For instance, there are Slater Type Orbitals (STOs), Gaussian orbitals, polynomials, and mixed bases, that span the global physical space under investigation and for many applications a Global Basis Set (GBS) is sufficient. There are however some cases of interest where these functions are not sufficiently accurate and should be either modified, or in some cases abandoned, to obtain reasonable results from computations. One such case is the spatially confined atom problem [12, 11].

Spatial confinement is the process of restricting the motion of atoms by manipulation of their environment [8]. Consider, for example, an atom trapped in a fullerene cage [17, 23, 10], or trapped on a semiconducting surface [16, 22], or embedded in a crystalline matrix or liquid host (quantum dot), or an atom under external pressure. During recent years, the realisation of such systems in the form of nano and molecular

electronic circuits has generated considerable interest in the development of the idea of quantum confinement. Models of confinement are thus important to study, as they reveal the affect of spatial restriction on the complex electron-electron and nucleus-electron interaction, as well as providing tests of existing mathematical models, methods, and their approximations to electronic structure under extreme conditions.

The affect of confinement on electronic structure is usually studied by considering a single atom or molecule at the centre of a sphere with a potential imposed on the surface of the sphere [16, 22, 23, 25, 5, 26, 10, 13]. The respective confinement potential usually considered is,

$$v(r) = \begin{cases} -\frac{Z}{r} & r < r_c \\ v_c(r) & r \geq r_c \end{cases}, \quad (1)$$

where  $r_c$  is a given cutoff radius and  $v_c$  is a supplementary potential often considered to be a constant. For radii less than the cutoff radius, the potential is the familiar coulomb potential with the nuclear charge  $Z \in \{\mathbb{Z}^+\}$ . Both Hartree-Fock (HF) and Kohn-Sham methods have been used that effectively cancel out the electron statefunction (or density function) on the surface of the sphere on  $r_c$  with  $v_c(r) = \infty$ . To study that model of confinement, modified STOs can provide a sufficiently accurate basis [18].

A more realistic approach corresponds to a soft, penetrable wall on the surface of the sphere in which the electron statefunction (or density function) can tunnel through the surface of the sphere and into the

classically forbidden region [19, 17, 20, 21]. In these cases and especially in considering more structurally complex potentials than (1), it is difficult to propose a suitable GBS, or a suitable GBS is unknown. An alternative to a GBS is a Local Basis Set (LBS) that does not impose any specific restrictions on the geometric form of the statefunction, though very few works on the HF method for the many-electron atom can be found at this time [1, 7, 6, 27, 28]. In particular, a comparison between global, modified STOs and LBSs of a finite element (FE) type within HF's method has been explored in some detail for highly spatially confined He [28].

The purpose of this work, as laid out in Section 2, is to present for the first time the theoretical and computational details of our implementation of HF's method for the many-electron atom in a FE basis. Following that, in Section 3, several numerical experiments are performed using our own home-brewed code with the aim of testing the accuracy of the HF statefunctions determined by LBSs. To that end, computations are performed for a selected number of atoms and ions as well as for the spatially confined atom problem for helium. The results are shown to be competitive with those of the HF and Roothaan-Hartree-Fock (RHF) GBS approaches of Bunge *et al.* [4, 3] and Koga *et al.* [14, 15]. Finally, this contribution is summarised in Section 4 and an outlook for future directions of research is delivered.

## 2 Method of computation

In this section the HF method is first described in brief (below) and then the formalism is written using Galerkin's FE method a spherical coordinate system. Some details of the algorithm and computational procedures are included for completeness. Specifically, we are interested in the accurate computation of the total energy expressed as,

$$\varepsilon = \varepsilon_{ke} + \varepsilon_v + \varepsilon_H + \varepsilon_x, \quad (2)$$

which is the sum of the kinetic energy, the nuclear-electron energy, the direct (Hartree), and the exchange energy. The kinetic energy and nuclear-electron energy are respectively,

$$\varepsilon_{ke} = -\frac{1}{2} \int \psi_a^*(x) \Delta_x \psi_a(x) dx, \quad (3)$$

and

$$\varepsilon_v = \int \psi_a^*(x) v(x) \psi_a(x) dx, \quad (4)$$

where  $\Delta$  is the Laplace operator and  $v(x)$  is an as of yet unspecified electrostatic potential. The direct term is,

$$\varepsilon_H = \iint \psi_a^*(x_1) \psi_a(x_1) \frac{1}{r_{12}} \psi_b^*(x_2) \psi_b(x_2) dx_1 dx_2, \quad (5)$$

and the exchange term is,

$$\varepsilon_x = \iint \psi_a^*(x_1) \psi_b(x_1) \frac{1}{r_{12}} \psi_a(x_2) \psi_b^*(x_2) dx_1 dx_2, \quad (6)$$

$r_{12} = |x_1 - x_2|$  is a radial distance and the summation of electron states  $N = \{a, b, \dots\}$  is implied. Note, that the exchange integral (6) is a non-local integral and is challenging to compute.

The electron statefunctions  $\psi \in \mathbb{C}$  are constrained by the orthonormalisation condition,

$$\int \psi_a^*(x) \psi_b(x) dx = \delta_{ab}. \quad (7)$$

and are determined by the variational principle (Rayleigh-Ritz approximation) that minimises,

$$\varepsilon = \frac{\int \psi^*(x) \hat{H} \psi(x) dx}{\int \psi^*(x) \psi(x) dx} \quad (8)$$

and the absolute error of the energy,

$$\eta(\varepsilon) = \frac{\delta \varepsilon}{\delta \psi} \leq \mathcal{T}, \quad (9)$$

up to a specified tolerance,  $\mathcal{T}$ .

### 2.1 Grid-based Hartree and Fock method

First consider the simplest many-electron case in which the principle shell,  $n = \{1, 2, \dots\}$ , and sub-shell of the atom, for angular momentum states,  $\ell = \{0, 1, 2, \dots\} = \{s, p, d, \dots\}$ , are filled. We refer to these atomic configurations, written explicitly in Table 1, as closed sub-shell atoms. In this picture, the atomic system has spherical symmetry and thus can be solved in a spherical coordinate system.

Spherical symmetry is equivalent to a special and convenient choice of electron statefunctions, that are decomposed into components of radial, angular, and spin,

$$\psi_a(x) = \frac{P_{n_a \ell_a}(r)}{r} Y_{\ell_a m_a}(\Theta) \chi_{\uparrow \downarrow}, \quad (10)$$

where  $P_{n_a \ell_a}$  are radial (state) functions,  $Y_{\ell_a m_a}$  are spherical harmonics,  $\Theta = (\theta, \phi)$ , and  $\chi_{\uparrow \downarrow}$  is an internal spin-up/spin-down degree of freedom. The quantum numbers  $\{n, \ell, m\}$  describe the shell and sub-shell structure of the atom. Here, the sum over the

magnetic quantum number  $m$  is carried out explicitly, where,

$$\sum_m \leftarrow 2(2\ell + 1), \quad (11)$$

for a given  $\ell$  and states are spin degenerate. Thus, the number of quantum numbers required to describe the shell structure of the atom reduces to two; namely, the principle quantum number  $n$ , and the angular momentum quantum number  $\ell$ .

A good choice of FE *ansatz*, defined with the lo-

cal FE interpolation polynomials  $\varphi(r) \in \mathbb{R}$ , is,

$$P_{n_a \ell_a} = \sum_j u_j(n_a \ell_a) \varphi_j(r), \quad (12)$$

where Latin indices  $j$  label degrees of freedom and  $u \in \mathbb{R}$  is a vector of coefficients to be determined. Note, that the interpolation polynomials are independent of both quantum numbers  $n$  and  $\ell$ .

Making the transformation to a spherical coordinate system and making use of (10) and (12), the single non-interacting electron energy integral, that corresponds to Schrödinger's equation is,

$$I_h(n_a \ell_a) = \int \sum_{ij} \left[ \frac{1}{2} \nabla \varphi_i(r) \nabla \varphi_j(r) + \frac{\ell_a(\ell_a + 1)}{2r^2} \varphi_i(r) \varphi_j(r) + v(r) \varphi_i(r) \varphi_j(r) \right] u_i(n_a \ell_a) u_j(n_a \ell_a) dr. \quad (13)$$

and with the definition of the interaction term,

$$[R_h]_L(a, b, c, d) = \iint [G_h]_L(a, b, c, d) dr_1 dr_2 \quad (14)$$

where

$$[G_h]_L(a, b, c, d) = \sum_{ij} \varphi_i(r_1) \varphi_j(r_1) u_i(n_a \ell_a) u_j(n_c \ell_c) \sum_{kl} \varphi_k(r_2) \varphi_l(r_2) \frac{r_{<}^L}{r_{>}^{L+1}} u_k(n_b \ell_b) u_l(n_d \ell_d), \quad (15)$$

and  $r_{<} = \min[r_1, r_2]$  and  $r_{>} = \max[r_1, r_2]$ , the total HF energy is expressed as,

$$\varepsilon = \sum_{n_a \ell_a} \left[ I_h(n_a \ell_a) + \sum_{n_b \ell_b} (2\ell_b + 1) \left( [R_h]_0(n_a \ell_a, n_b \ell_b, n_a \ell_a, n_b \ell_b) + \sum_L \Lambda_L [R_h]_L(n_a \ell_a, n_b \ell_b, n_b \ell_b, n_a \ell_a) \right) \right], \quad (16)$$

Table 1: Closed sub-shell atomic configurations of neutral atoms with  $Z \leq 54$ .

$N$	element	configuration
2	He	1s <sup>2</sup>
4	Be	[He]2s <sup>2</sup>
10	Ne	[He]2s <sup>2</sup> 2p <sup>6</sup>
12	Mg	[Ne]3s <sup>2</sup>
18	Ar	[Ne]3s <sup>2</sup> 3p <sup>6</sup>
20	Ca	[Ar]4s <sup>2</sup>
30	Zn	[Ar]3d <sup>10</sup> 4s <sup>2</sup>
36	Kr	[Ar]3d <sup>10</sup> 4s <sup>2</sup> 4p <sup>6</sup>
38	Sr	[Kr]5s <sup>2</sup>
48	Cd	[Kr]4d <sup>10</sup> 5s <sup>2</sup>
54	Xe	[Kr]4d <sup>10</sup> 5s <sup>2</sup> 5p <sup>6</sup>

where the summation,

$$\sum_L := \sum_{|\ell_a - \ell_b|}^{\ell_a + \ell_b}, \quad (17)$$

is implied and the lambda symbol represents a function of the familiar Wigner 3j-symbol,

$$\Lambda_L = -\frac{1}{2} \begin{pmatrix} \ell_a & L & \ell_b \\ 0 & 0 & 0 \end{pmatrix}^2. \quad (18)$$

Note, that with the potential,  $v_c(r) = \infty(1)$ , the state-functions are supplemented with zero-valued Dirichlet boundary constraints defined by,  $P_{n_a \ell_a}(r) = 0$  where  $r \in \{0, r_c\}$ .

The problem at hand has now become the problem of finding  $N = \{a, b, \dots\}$  eigenpairs  $\{\varepsilon_a, u_a\} \in$

$\mathbb{R}$  that satisfy the generalised eigenspectrum problem,

$$\left[ A - \varepsilon_a B \right] u_a = 0, \quad (19)$$

where  $A$  is the system matrix generated by the Hamiltonian  $\hat{H}$  and,

$$B = \int \sum_{ij} \varphi_i(r) \varphi_j(r) dr, \quad (20)$$

is the mass (or overlap) matrix.

## 2.2 Computational details

The general form of a self-consistent algorithm is well known. The procedure for the HF method starts from the initial conjection of either the electron energies or statefunctions. These initial quantities are then used to assemble and solve the generalised eigenspectrum (19) in successive iterations labelled,  $n = 1, \dots, n_{\max}$ , until the energy and statefunctions remain unchanged up to a specified tolerance,  $\mathcal{T}$ .

A crucial observation taken from the description of the HF method in Galerkin's FE basis lead to a number of simplifications of the standard algorithmic procedure. Specifically, if the FE grid does not change throughout the self-consistent procedure, then naturally, integrals over the FE space are constant throughout the self-consistent procedure. With these observations, the generalised eigenspectrum problem (19) can be written,

$$\left[ I + F^n - \varepsilon_a^n B \right] u_a^n = 0, \quad (21)$$

where  $F^n$  depends on the Wigner  $3j$ -symbol, the coefficient vectors  $u_a^{n-1}$ , and the FE integral tensor,

$$G_{L,ijkl} = \sum_{ijkl} \varphi_i(r_1) \varphi_j(r_1) \varphi_k(r_2) \varphi_l(r_2) \frac{r_{<}^L}{r_{>}^{L+1}}. \quad (22)$$

In the generalised eigenspectrum problem (21), the matrix  $I$  of the single non-interacting electron integral (cf. (13)), the mass matrix  $B$  (cf. (20)), and the FE integral tensor (22), are constant and are required to be assembled *once only* at the start of the self-consistent procedure.

The resultant self-consistent algorithm is described in Algorithm 1. In short, the algorithm starts from assembling the constant objects in (21), as discussed above, and continuing with iteratively solving the generalised eigenspectrum problem in the basis of matrices, eigenvalues, and coefficient eigenvectors until the specified convergence specified convergence criteria are met.

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**Algorithm 1** A psuedocode description of the self-consistent algorithm described in Section 2.2.

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**Require:**  $Z, v(r)$  ▷ physical quantities  
**Require:**  $n_{\max}, \eta(\varepsilon)$  ▷ convergence criteria

- 1: **for**  $n \leftarrow 0$  **to**  $n_{\max}$  **do**
- 2:     **if**  $n = 0$  **then**
- 3:         assemble:  $I$  and  $B$  ▷ cf. (13) and (20)
- 4:         assemble:  $G_{L,ijkl}$  ▷ cf. (22)
- 5:          $F^n \leftarrow 0$
- 6:     **else**
- 7:         assemble:  $F^n$
- 8:     **end if**
- 9:      $A^n \leftarrow I + F^n$
- 10:     solve:  $\left[ A^n - \varepsilon_a^n B \right] u_a^n = 0$
- 11:     compute:  $\varepsilon^n$  ▷ cf. (16)
- 12:     **if**  $n \neq 0$  **then**
- 13:          $\eta(\varepsilon) \leftarrow |\varepsilon^{n-1} - \varepsilon^n|$
- 14:         **if**  $\eta(\varepsilon) \leq \mathcal{T}$  **then**
- 15:              $n \leftarrow n_{\max}$  ▷ **break**
- 16:         **else**
- 17:              $n \leftarrow n + 1$
- 18:         **end if**
- 19:     **end if**
- 20: **end for**

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In the numerical experiments that follow, a FE grid was generated by placing the vertices of FE cells at positions  $g_i$  where  $i \in \mathbb{Z} = \{0, 1, \dots, \#K\}$ , according to the formula [24, 28],

$$g_i = \begin{cases} 0 & i = 0 \\ \frac{\exp(\beta i - 1) - 1}{\exp(\beta \#K) - 1} r_{\max} & \text{otherwise} \end{cases}, \quad (23)$$

where  $\beta = \log(\alpha) / (\#K - 1)$  and  $\alpha = 200$  is a constant. Naturally, the grid generator (23) results in a grid that is denser close to the origin and sparser as it tends toward the boundary,  $r_{\max}$ . For practical computations of free atoms and ions and presented below, the value  $r_{\max} = 50$  was found to be sufficiently large to correctly describe the statefunctions in the asymptotic region.

## 3 Numerical experiments

In this section the grid-based LBS method described in Section 2 is implemented first for a variety of free atoms, then for a series of ions, and finally for the spatially confined atom problem described in Section 1.

It is worth remarking that our method is based on a variational principle, which is an indispensable facet

of the model in order to find the wanted statefunctions. The main issue is to obtain highly accurate HF statefunctions through carefully controlled and stabilised self-consistent convergence of the HF energy. Our interest comes from an ambition to apply the scheme to accurate predictions of the atomic spectra of highly correlated spatially confined electron motion in the near future. Naturally, to perform those computations, high quality HF statefunctions are required to start from. Furthermore, for accurate predictions of the atomic spectra so-called 'chemical accuracy' is required, which has an absolute tolerance in the HF energy of,  $\eta_{\text{abs}}(\varepsilon) \leq 1 \text{ meV} \sim \mathcal{O}(10^{-5})$  Hartrees.

### 3.1 Free atoms and ions

Let us consider first closed sub-shell atomic configurations, where the corresponding potential for the free atom is,

$$v(r) = -\frac{Z}{r}. \quad (24)$$

The atomic sub-shells are filled in the configurations presented in Table 1. In convergence tests, the largest atom considered here, Xe ( $Z = 54$ ), was found to exhibit good convergence behaviour up to  $\mathcal{T} \leq \mathcal{O}(10^{-12})$  with an FE space with  $\#K = 12$  and 9th-order interpolation polynomials. It is worth remarking, that higher-order polynomials are preferred in order to obtain high quality state-functions in regions far from the atomic nucleus where smooth, exponential decay of the statefunctions is observed, cf. Ref. [28, 9]. Additionally, we remark, that the computation of Xe requires simultaneous support for five s-states, four p-states, and two d-states. The HF energy up to 6 decimal places  $\varepsilon_{\text{Xe}} = -7232.138534$  can be compared to that of Bunge *et al.* [4] and Koga *et al.*, [15] who obtain  $\varepsilon_{\text{Xe}} = -7232.138363$  and  $\varepsilon_{\text{Xe}} = -7232.138364$  respectively. Clearly, we are obtaining good quality statefunctions for Xe.

Note, that it is not guaranteed that this FE space will provide optimised support for lighter atoms with  $Z \leq 54$  (though this was found to be the case) since variations in the nuclear charge  $Z$  naturally affect the frequency of oscillation of the corresponding statefunctions. To have confidence in this, the convergence of Ar ( $Z = 18$ ) are examined in Table 2 where the relative error is defined,  $\eta_{\text{rel}}(\varepsilon^n) = \varepsilon^{n-1} - \varepsilon^n$ . In general it is important, though not necessary, that self-consistent convergence is obtained from above, meaning, that  $\eta_{\text{rel}} \geq 0$ . This was found to be the case for all free atoms considered, where the mixing parameter was set to  $\alpha = 0.9$ .

The respective HF energies and sub-shell energy eigenvalues for closed sub-shell atoms with  $Z \leq 54$

Table 2: Convergence of the total HF energy with respect to self-consistent cycles  $n$  for Ar.

$n$	$\varepsilon_{\text{Ar}}^n$	$\eta_{\text{rel}}^n(\varepsilon)$
1	-450.646 748 116	-450.646 748 116
2	-514.572 745 355	-63.925 997 238
3	-525.155 772 285	-10.583 026 930
4	-526.632 846 894	-1.477 074 609
5	-526.798 350 478	-0.165 503 583
6	-526.815 566 162	-0.017 215 684
7	-526.817 316 273	-0.001 750 111
8	-526.817 492 998	-0.000 176 725
9	-526.817 510 808	-0.000 017 809
10	-526.817 512 601	-0.000 001 793
11	-526.817 512 782	-0.000 000 180
12	-526.817 512 800	-0.000 000 018
13	-526.817 512 803	-0.000 000 001
14	-526.817 512 803	-0.000 000 000

are presented in Table 3. The HF energies can be compared to those extensively tabulated by Koga *et al.* [15] evaluated with RHF statefunctions. Their results, presented up to ten significant figures, are an improvement over some previous works [4, 14]. First, we note that the HF energies computed with  $Z \leq 30$  agree exactly with those of Koga *et al.* with differences  $\mathcal{O}(10^{-6})$  for Kr and Sr. The largest difference is on the 4th decimal place for Xe, which is a small but significant difference, since our variational result is slightly *lower* in energy.

Problematically, at this time we have not found any previous computations of the energy eigenvalues are reported up to 9 decimal places, and hence we compare the energy eigenvalues with those of Bunge *et al.* [3], written up to chemical accuracy. In every case the minimal demand of chemical accuracy is satisfied and, in some cases, we have obtained slightly lower energy eigenvalues. For instance, the largest difference comparing the energy eigenvalues in Table 3 and in Ref. [3] show an improvement to  $\mathcal{O}(10^{-4})$  Hartrees.

A more difficult problem to solve computationally than the free neutral atom, is to consider the computation of free ions. One way to compute the electronic structure of ions is to manipulate the nuclear charge. For instance, the negative ion  $\text{H}^-$  is equivalent the computation of He with  $Z = 1$  and the positive ion  $\text{Li}^+$  is equivalent to the computation of He with  $Z = 3$ . The ground-state of some stable ions are collected in Table 4. Here, convergence from above was only guaranteed where the mixing parameter was set to the lower value,  $\alpha = 0.75$ , which increased the

Table 3: Total HF energy and orbital energy values for atoms in the first five periods of the periodic table of the elements. Underlined digits denote energy differences, cf. [15]. For all atoms considered the virial ratio is satisfied.

$Z$	element	$\varepsilon$	$n$	$s (\ell = 0)$	$p (\ell = 1)$	$d (\ell = 2)$
2	He	-2.861 679 996	1	-0.917 955 562		
4	Be	-14.573 023 168	1	-4.732 669 894		
			2	-0.309 269 551		
10	Ne	-128.547 098 109	1	-32.772 442 802	-0.850 409 653	
			2	-1.930 390 883		
12	Mg	-199.614 636 424	1	-49.031 736 070	-2.282 226 016	
			2	-3.767 721 465		
			3	-0.253 052 581		
18	Ar	-526.817 512 803	1	-118.610 350 558	-9.571 465 562	
			2	-12.322 153 311	-0.591 017 411	
			3	-1.277 353 027		
20	Ca	-676.758 185 925	1	-149.363725889	-13.629 269 203	
			2	-16.822 744 270	-1.340 706 953	
			3	-2.245 376 002		
			4	-0.195 529 691		
30	Zn	-1777.848 116 297	1	-353.304 542 396	-38.924 841 351	-3.839 374 125
			2	-44.361 721 863	-0.782 537 479	
			3	-5.637 816 573		
			4	-0.292 507 211		
36	Kr	-2752.054 978 <u>746</u>	1	-520.165 471 119	-63.009 786 743	-3.825 234 975
			2	-69.903 083 616	-8.331 502 060	
			3	-10.849 467 123	-0.524 186 782	
			4	-1.152 935 248		
38	Sr	-3131.545 689 <u>310</u>	1	-583.687 886 884	-72.996 037 443	-5.694 395 091
			2	-80.390 795 627	-10.699 975 673	
			3	-13.475 028 674	-1.098 162 609	
			4	-1.896 811 438		
			5	-0.178 456 308		
48	Cd	-5465.133 191 <u>723</u>	1	-955.315 401 230	-132.047 019 267	-16.071 970 993
			2	-142.006 829 830	-23.597 233 527	-0.763 657 206
			3	-27.708 623 087	-3.053 504 065	
			4	-4.450 534 706		
			5	-0.264 855 826		
54	Xe	-7232.138 <u>534 464</u>	1	-1224.397 939 313	-177.782 449 002	-26.118 868 897
			2	-189.340 136 110	-35.221 661 669	-2.777 880 779
			3	-40.175 665 284	-6.008 338 139	
			4	-7.856 302 125	-0.457 290 051	
			5	-0.944414425		

Table 4: HF energies for a selected number of ions. Underlined digits denote energy differences, cf. [15].

$Z$	element	$\varepsilon^+$	$\varepsilon^-$
1	H <sup>-</sup>		-0.487 930
3	Li <sup>±</sup>	-7.236 415	-7.428 232
5	B <sup>+</sup>	-24.237 575	
9	F <sup>-</sup>		-99.459 454
11	Na <sup>±</sup>	-161.676 961	-161.855 126
13	Al <sup>+</sup>	-241.674 670	
17	Cl <sup>-</sup>		-459.576 925
19	K <sup>±</sup>	-599.017 579	-599.161 917
21	Sc <sup>+</sup>	-759.462 097	
29	Cu <sup>-</sup>		-1638.964 145
31	Ga <sup>+</sup>	-1923.059 723	
35	Br <sup>-</sup>		-2572.536 273
37	Rb <sup>±</sup>	-2938.219 932	-2938.354 901
39	Y <sup>+</sup>	-3331.472 886	
47	Ag <sup>-</sup>		-5197.700 089
49	In <sup>+</sup>	-5739.978 454	
53	I <sup>-</sup>		-6918.076 024
55	Cs <sup>+</sup>	-7553.810 532	

number of iterations in self-consistent procedure by a few cycles. Nevertheless, clearly, good quality statefunctions are found in almost all cases. For instance, the seemingly large differences for Ag<sup>-</sup>, I<sup>-</sup>, and Sc<sup>+</sup> possibly arise from a coincidental numerical round-off (compare our result with that of Koga *et al.* [15], where the value is,  $\varepsilon_{\text{Ag}^-} = -5197.698473$ ).

Another possible explanation for these differences is, that our interpretation of the electron structure does not correspond to the physical one; for instance, the electronic structure of Sc<sup>+</sup> was assumed to equivalent to Ca with  $Z = 21$ . Nevertheless, our computation of the HF energy yields,  $\varepsilon_{\text{Sc}^+} = -759.462097$  which compared to the value of Koga *et al.* [15] of  $\varepsilon_{\text{Sc}^+} = -759.735718$  is a difference of 0.03% of the total energy. These anomalous results are open for future investigation and refinement.

Another measure of the quality of the statefunctions is the virial ratio,

$$\xi = -\frac{\varepsilon - \varepsilon_{\text{ke}}}{\varepsilon_{\text{ke}}} = -\frac{\varepsilon_{\text{pe}}}{\varepsilon_{\text{ke}}} = 2. \quad (25)$$

It was found (not shown here) that for all atoms in Table 3 and ions in Table 4, that the virial ratio is satisfied, to  $\eta(\xi) \leq \mathcal{O}(10^{-9})$ .

### 3.2 Spatially Confined helium

Here we consider the spatially confined atom problem for He [2] with the corresponding potential (1)

with  $v_c(r) = \infty$ . Naturally, this implies zero-valued Dirichlet boundary constraints at  $r = \{0, r_c\}$  and the only remaining grid parameter is  $r_{\text{max}} = r_c$ . Values of the cutoff radius  $r_c$  considered here are chosen to coincide with the supplementary material of Young *et al.* [28] for the comparison with a different implementation of Galerkin's FE basis as well as with the GBS (modified STOs) used there. For these computations, the tolerance on self-consistent determination of the HF energy is set to,  $\mathcal{T} \leq \mathcal{O}(10^{-9})$ .

Here, we are interested in the HF energy  $\varepsilon$ , the direct energy  $\varepsilon_{\text{H}}$ , the exchange energy  $\varepsilon_{\text{X}}$ , and the virial ratio  $\xi \leq 2$ , cf. (25). These quantities and moments of the general form,

$$\langle r^k \rangle = \int \psi_a^*(r) r^k \psi_a(r) dr, \quad (26)$$

are collected in Table 5 for  $k \in \{-1, 1, 2\}$ . Naturally,  $\langle r^0 \rangle_a = 1$ , cf. (7) and is satisfied to within  $\mathcal{O}(10^{-9})$  for all computed statefunctions at all confinement radii considered.

One point of interest is the HF energy at the extreme cutoff radius  $r_c = 0.1$ . Here, the HF energy is computed to be  $\varepsilon_{\text{he}} = -906.616396$  whereas Young *et al.* find  $\varepsilon_{\text{he}} = -906.616349$  with a GBS, which is a small difference of  $4 \times 10^{-5}$ . This is the largest difference occurring from the set of HF energies analysed from Table 5, with all other differences  $\eta(\varepsilon) \leq \mathcal{O}(10^{-6})$ . Additionally, there is an improvement over the LBS presented there in Ref.[28] by two orders of magnitude. Clearly, we are obtaining good quality statefunctions and energies to within the wanted chemical accuracy.

Another point of general interest is the critical spatial confinement radius, for which the HF energy  $\varepsilon = 0$  and the virial ratio  $\xi = 1$ . By using the method of bisection, we report, that the critical spatial confinement radius for He was found to be  $r_c = 1.106448$ . This value can be verified by GBS in future numerical analyses.

## 4 Summary

In this contribution, our implementation of HF's method in a spherical coordinate system was introduced for the first time in some detail. It was shown, that the HF statefunctions can be accurately determined by means of LBSs of the FE type. Unlike with GBSs, the grid on which the statefunctions are represented was not changed for the computation ground-state of atoms and for ions with  $Z \leq 54$ . This, plus the fact that the only restrictions of the statefunctions are boundary constraints, mean that the method is attractive for seeking the HF statefunctions for more

Table 5: HF, and direct and exchange components of the HF energy and the virial ratio computed for the spatially confined atom problem for He at a variety of cutoff radii  $r_c$ . Moments (26) of the HF statefunction are also shown.

$r_c$	$\varepsilon$	$\varepsilon_H$	$\varepsilon_x$	$\xi$	$\langle r^{-1} \rangle$	$\langle r^1 \rangle$	$\langle r^2 \rangle$
0.1	906.616 396	36.084 203	-18.042 101	0.082 068	24.774 698	0.049 501	0.002779
0.2	206.204 532	18.235 120	-9.117 560	0.166 789	12.598 736	0.097 968	0.010925
0.3	82.386 229	12.293 793	-6.146 896	0.253 981	8.548 825	0.145 347	0.024136
0.4	41.030 936	9.329 884	-4.664 942	0.343 393	6.530 847	0.191 581	0.042093
0.5	22.790 953	7.557 347	-3.778 673	0.434 695	5.325 984	0.236 612	0.064462
1.0	1.061 202	4.063 502	-2.031 751	0.902 610	2.966 756	0.441 719	0.229769
1.2	-0.664 622	3.504 695	-1.752 347	1.083 432	2.595 746	0.513 396	0.313 57
1.4	-1.574 173	3.119 000	-1.559 500	1.252 371	2.342 796	0.578 614	0.402630
1.6	-2.084 225	2.842 489	-1.421 244	1.404 635	2.164 083	0.637 152	0.493771
1.8	-2.382 684	2.639 456	-1.319 728	1.536 913	2.035 038	0.688 927	0.584048
2.0	-2.562 580	2.488 243	-1.244 121	1.647 758	1.940 694	0.734 012	0.670873
3.0	-2.831 049	2.142 374	-1.071 187	1.931 449	1.735 410	0.871 768	0.998758
3.5	-2.851 875	2.089 878	-1.044 939	1.973 162	1.706 834	0.900 880	1.087268
4.0	-2.858 588	2.066 843	-1.033 421	1.990 038	1.694 840	0.915 588	1.137639
5.0	-2.861 388	2.053 641	-1.026 820	1.998 781	1.688 271	0.925 358	1.175798
6.0	-2.861 654	2.051 786	-1.025 893	1.999 867	1.687 395	0.927 011	1.183417
7.0	-2.861 677	2.051 564	-1.025 782	1.999 986	1.687 293	0.927 241	1.184636
8.0	-2.861 680	2.051 540	-1.025 770	1.999 998	1.687 283	0.927 269	1.184804
9.0	-2.861 680	2.051 538	-1.025 769	1.999 999	1.687 282	0.927 272	1.184825
10.0	-2.861 680	2.051 538	-1.025 769	1.999 999	1.687 282	0.927 273	1.184827
25.0	-2.861 680	2.051 538	-1.025 769	1.999 999	1.687 282	0.927 273	1.184827

complex examples of the potential (1) describing the atom's environment. The results presented for free atoms and ions show that local LBSs are a competitive alternative to GBSs and can reproduce HF statefunctions with the same or superior quality as the RHF statefunctions presented by Bunge *et al.* [4, 3] and Koga *et al.* [14, 15]. The results presented for the spatially confined He are also an improvement on the previous grid-based implementation of Young *et al.* [28].

From here, we will continue with this implementation of HF's method using LBS of the FE type and consider the method for heavier atoms under extreme spatial confinement and with the more involved supplementary potential,  $v_c(r) = [0, \infty)$ , as well as post-HF methods that include correlated electron motion.

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