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Application of Combined Hartree-Fock-Roothaan Theory to Isoelectronic Series of Atoms Using Noninteger n-Generalized Exponential Type Orbitals

I. I. Guseinov, M. Ertürk

Department of Physics, Faculty of Arts and Sciences, Onsekiz Mart University, Çanakkale, Turkey

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Abstract

We investigate the efficiency of noninteger n-generalized exponential type orbitals in energy calculations of isoelectronic series of atoms from Be to Ne and K [Ar]$4s^0 3d^1$ (^2D) and Cr^+ [Ar]$4s^0 3d^5$ (^6S) using combined Hartree-Fock-Roothaan theory. The results of calculations are compared with the values obtained in literature. All of the nonlinear parameters are fully optimized. It is shown that the use of noninteger n-generalized exponential type orbitals in atomic electronic structure calculations gives the superior agreement with numerical Hartree-Fock calculations. The minimum energy error, which is 0.00204432 Hartree, is observed for the neutral Be atom with respect to corresponding numerical Hartree-Fock result.

1. Introduction

It is well known that the Hartree-Fock-Roothaan (HFR) methods are widely used in calculation of electronic structure of closed and some open shell multi-electron systems [1-3]. These methods are not suitable for an arbitrary open shell electronic configuration [4-14] due to the off-diagonal multipliers because they, in general, cannot be eliminated. In the previous works [15, 16], by the use of principle of indistinguishabilty of identical particles, all of the insufficiencies arising in Roothaan's open shell Hartree-Fock (HF) theory have been eliminated. In these papers, the combined open shell HF and HFR equations for atomic-molecular and nuclear systems applicable to any multideterminantal state of a single configuration that has any number of open shells of any symmetry were suggested. The open shell combined Hartree-Fock-Roothaan (CHFR) theory [15-19], in which the problem of the off-diagonal multipliers does not arise, has been applied and tested successfully for some arbitrary open shells atoms in nonrelativistic electronic structure calculations. In order to solve the open shell atomic CHFR equations, one must expand the atomic orbitals as linear combination of basis functions. Accuracy of total energy calculations and computational cost directly depend on the quality of the chosen atomic basis sets. Therefore, it is desirable to use the exponential type atomic orbitals in atomic calculations because they satisfy the cusp condition at the nuclei [20] and the exponential decay for large distances [21].

It is well known that, in atomic structure calculations, the Slater type orbitals (STO) and Gaussian type orbitals (GTO) as basis functions are currently used. The STO and GTO are defined by [22, 23]

$$\chi_{n^*lm}\left(\zeta,\vec{r}\right)=\frac{\left(2\zeta\right)^{n^*+\frac{1}{2}}}{\left[\Gamma\left(2n^*+1\right)\right]^{\frac{1}{2}}}r^{n^*-1}e^{-\zeta r}S_{lm}\left(\theta,\varphi\right) \tag{1}$$

and

$$\Omega_{nlm}\left(\zeta,\vec{r}\right)=\frac{2^{n+1}\zeta^{(2n+1)/4}}{\left[(2n-1)!!\right]^{\frac{1}{2}}\left(2\pi\right)^{1/4}}r^{n-1}e^{-\zeta r^2}S_{lm}\left(\theta,\varphi\right), \tag{2}$$

respectively. In these equations, $\Gamma\left(x\right)$ and $S_{lm}\left(\theta,\varphi\right)$ are the gamma function and complex or real spherical harmonics, respectively; $\zeta>0$ is the orbital exponent. Conventional integer n-STO (ISTO) assume that the principal quantum number n^* in Eq. (1) is positive integer ($n^*\equiv n$) and, hence, in this case $\Gamma\left(2n^*+1\right)=\left(2n^*\right)!$. However, the noninteger *n*-STO (NSTO) which considerably improves the description of electronic structure [24-36] is also used as basis functions in atomic HFR calculations. During the past decade, the NSTO basis sets for atoms have been prepared by Koga [31-36] using the traditional HFR method. The accuracy of these basis sets can be measured by comparison with numerical Hartree-Fock (NHF) results which are available in literature.

The subject of the quality of basis sets, because of its important role in electronic structure calculations, has received much attention in literature. In order to improve the quality of given basis sets, many different modified basis sets have been proposed. To obtain the best values of physical properties for atoms and their ions, such as nuclear quadrupole coupling constant, nuclear magnetic shielding, diamagnetic susceptibility, electric field gradient, etc., use of the accurate wave functions, appearing in basis sets approach, is of fundamental importance in the study of electronic structure calculations. For the quantitative descriptions of atomic electronic structure, the noninteger n-generalized exponential type orbitals (GETO) were proposed [37] and applied to HFR calculations within the minimal basis sets approximation. The normalized GETO are defined by

$$G_{n^*lm}\left(\zeta,\mu,\vec{r}\right)=\left\{\frac{\mu\left(2\zeta\right)^{\frac{2n^*+1}{\mu}}}{\left[\Gamma\left(\frac{2n^*+1}{\mu}\right)\right]}\right\}^{1/2} r^{n^*-1}e^{-\zeta r^{\mu}}S_{lm}\left(\theta,\varphi\right), \qquad (3)$$

where μ is the nonlinear parameter which can be determined by energy minimization.

In this work, using NSTO and GETO basis sets, the CHFR calculations have been performed for the neutral and 20 cationic members of the ground states energies for isoelectronic series of atoms from Be to Ne and, K [Ar]$4s^0 3d^1$ $\left({}^2D\right)$ (Z=19-30) and Cr^+ [Ar] $4s^0 3d^5$ $\left({}^6S\right)$ (Z=24-30). The quality of these basis sets are investigated and compared with NHF values. All of the nonlinear parameters are fully optimized. The total and orbital energies are in good agreement with those presented in the literature. Although the present calculations are nonrelativistic, the NSTO and GETO basis sets, in our opinion, can also be used in relativistic schemes. In Ref. [38], as a first step towards to this goal, the simple formulas for one- and two-electron one-center integrals over NSTO basis sets were derived in the quasi-relativistic approach. These integrals over GETO basis sets can also be described with the help of presented method. In presented approximation, all of these integrals reduced to some common integrals, which have to be calculated using NSTO or GETO functions. The computational method is described in the next section. Hartree atomic units used throughout this work.

2. Computational method

The CHFR calculation procedure, used in this work, was mainly described in our previous papers [17-19], where it was applied to atoms containing only s- and p-orbitals. Here, the calculations of energies for some heavy elements having the d-orbitals are also performed. All of the nonlinear parameters n^*, ζ and μ are determined by SCF optimization process using the quasi-Newton method.

According to CHFR theory, the expression of the energy functional in algebraic approximation is defined by

$$E = 2\sum_{q} (\rho h)_{qq} + \sum_{ij,kl} \sum_{pq} (2C_{ip}^{\dagger} A_{kl}^{ij} D_{kl}^{pq} C_{qj} - C_{ip}^{\dagger} B_{kl}^{ij} D_{kl}'^{pq} C_{qj}) , \tag{4}$$

where $\rho = CfC^{\dagger}$ and

$$D_{kl}^{pq} = (C^{\dagger} I^{pq} C)_{kl} , \tag{5}$$

$$D_{kl}'^{pq} = \left(C^{\dagger} K^{pq} C\right)_{kl} . \tag{6}$$

Here, f is the matrix of fractional occupancy of shells, h, I and K are the one-and two-electron matrices. The properties of coupling projection coefficients A_{kl}^{ij} and B_{kl}^{ij}, which are non-variable coefficients specific for the system under consideration, are described in Refs. [18, 19]. In atomic case, one-and two- electron integrals over the NSTO and GETO were evaluated in Refs. [32, 37, 39] by the use of relations in terms of the gamma and hypergeometric functions.

For the determination of optimum values of nonlinear parameters in GETO, the initial values of the nonlinear parameters were taken from the NSTO results [18, 19]. The values of nonlinear parameters obtained are, then, used in the optimization of GETO nonlinear parameters. We observed that the virial ratios do not deviate from the exact value of -2 by more than 1×10^{-7}. We notice that our optimizations in all of the calculations are sufficiently accurate.

Table 1. The NSTO and GETO total energies (E_{NSTO} and E_{GETO}), optimal μ parameters, total energy errors $\Delta E_{E_{NSTO}-E_{NHF}}$ and $\Delta E_{E_{GETO}-E_{NHF}}$ for the ground states ${}^4S$ of the N isoelectronic series (in Hartree)

Z	Atom	$-E_{NSTO}$ [18]	$-E_{GETO}$ (μ)	$\Delta E_{E_{NSTO}-E_{NHF}}$ [18]	$\Delta E_{E_{GETO}-E_{NHF}}$
7	N	54.356092199	54.370147822 (0.951714941)	0.044841980	0.030786357
8	O^{+1}	74.330134166	74.345020235 (0.956455368)	0.042471446	0.027585377
9	F^{+2}	97.567255764	97.582798343 (0.960381213)	0.041721792	0.026179213
10	Ne^{+3}	124.062503414	124.078572104 (0.963686585)	0.041711905	0.025643215
11	Na^{+4}	153.813178781	153.829675703 (0.966502351)	0.042114790	0.025617868
12	Mg^{+5}	186.817660577	186.834511471 (0.968927004)	0.042782537	0.025931642
13	Al^{+6}	223.074910581	223.092058300 (0.971033565)	0.043639398	0.026491680
14	Si^{+7}	262.584231835	262.601631732 (0.972879208)	0.044642996	0.027243099
15	P^{+8}	305.345138716	305.362755398 (0.974508157)	0.045768010	0.028151328
16	S^{+9}	351.357282382	351.375087405 (0.975956031)	0.046998438	0.029193414
17	Cl^{+10}	400.620405761	400.638375977 (0.977249613)	0.048323769	0.030353553
18	Ar^{+11}	453.134315237	453.152431586 (0.978413041)	0.049736786	0.031620437
19	K^{+12}	508.89886221	508.917108836 (0.979464909)	0.051232425	0.032985801
20	Ca^{+13}	567.913930744	567.932294324 (0.980419453)	0.052807019	0.034443439
21	Sc^{+14}	630.179429053	630.197898301 (0.981289632)	0.054457850	0.035988602
22	Ti^{+15}	695.695283535	695.713848812 (0.982086580)	0.056182869	0.037617592
23	V^{+16}	764.461434485	764.480087495 (0.982818079)	0.057980497	0.039327488
24	Cr^{+17}	836.477832958	836.496566517 (0.983492767)	0.059849510	0.041115952
25	Mn^{+18}	911.744438457	911.763246303 (0.984116049)	0.061788927	0.042981081
26	Fe^{+19}	990.261217184	990.280093830 (0.984695136)	0.063797969	0.044921323
27	Co^{+20}	1072.028140712	1072.047081321 (0.985232735)	0.065876002	0.046935394

3. Results and discussion

We have solved the atomic CHFR equations for the neutral and 20 cationic members of the ground state of isoelectronic series of atoms Be to Ne and, K [Ar]$4s^0 3d^1$ $\left({}^2D\right)$ and Cr^+

[Ar]$4s^0 3d^5$ $\left({}^6S\right)$ by using the expansion of single-particle radial wave function in terms of NSTO and GETO basis sets in algebraic approach. The coupling projection coefficients, used in the calculation of open shell electronic configurations, have been taken from Refs. [18, 19]. In the energy minimization process, we have restricted the exponential parameter μ to be common to all GETO basis sets. The total energies obtained from the NSTO, GETO and NHF calculations for the isoelectronic series of N (Z=7-27) atom are explicitly illustrated in Table 1. We see from this table, GETO results are about 1.5 times more accurate than NSTO. This feature is also observed for all the isoelectronic series of atoms examined in this work.

The GETO's total energy (E_{GETO}) errors ($\Delta E_{E_{GETO}-E_{NHF}}$) relative to the NHF values [40] for the isoelectronic series of Be to Ne are also shown in Figure 1. This figure shows that the E_{GETO} error curves are, in general, similar to those for NSTO total energy (E_{NSTO}) [18] relative to the NHF values. The $\Delta E_{E_{GETO}-E_{NHF}}$ in all calculations are not exceeded 0.200111221 Hartree which is observed for the neutral Ne atom. The minimum E_{GETO} error for the neutral Be atom within the isoelectronic series considered is obtained as 0.002044325 Hartree.

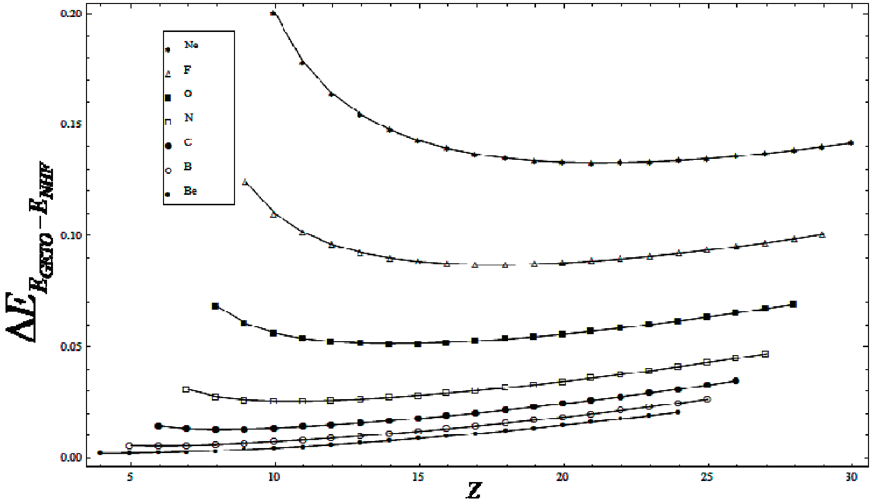

Fig. 1. The energy differences between E_{GETO} and E_{NHF} as a function of atomic number Z for isoelectronic series of the atoms Be to Ne (in Hartree)

The energy differences between E_{GETO} and E_{NSTO} ($\Delta E_{E_{NSTO}-E_{GETO}}$) for the isoelectronic series of Be to Ne are also shown in Figure 2. The $\Delta E_{E_{NSTO}-E_{GETO}}$ values in each isoelectronic series for Be to Ne are generally increased. It should be noted that we observed the small discrepancy between the GETO and NSTO basis sets of results from this figure, and this discrepancy seems to increase by increasing atomic number Z. In Ref. [37], Koga and Kanayama pointed out that the μ values constantly increase when the atomic number Z increases and, simultaneously, increase towards 1. Therefore, as we expect, the total energy differences between two basis sets decrease when the atomic number Z increases. As shown in figure 2, as not anticipated, the total energy errors always increase except the isoelectronic series of Be atom. This figure also shows that the GETO efficiency is better than in the case of NSTO especially with an increase in either the atomic number Z or in the number of electrons. An interesting feature observed in CHFR calculations for isoelectronic series using GETO basis sets is that the values of n^*_{1s} are larger than their nominal value ($n_{1s} \equiv 1$) and constantly increase when Z increases. The variations of optimal values of principal quantum number are determined as $1.001712671 \le n^*_{1s} \le 1.021633251$, $2.253168391 \le n^*_{2s} \le 2.746353776$ and $1.649153722 \le n^*_{2p} \le 1.968191279$.

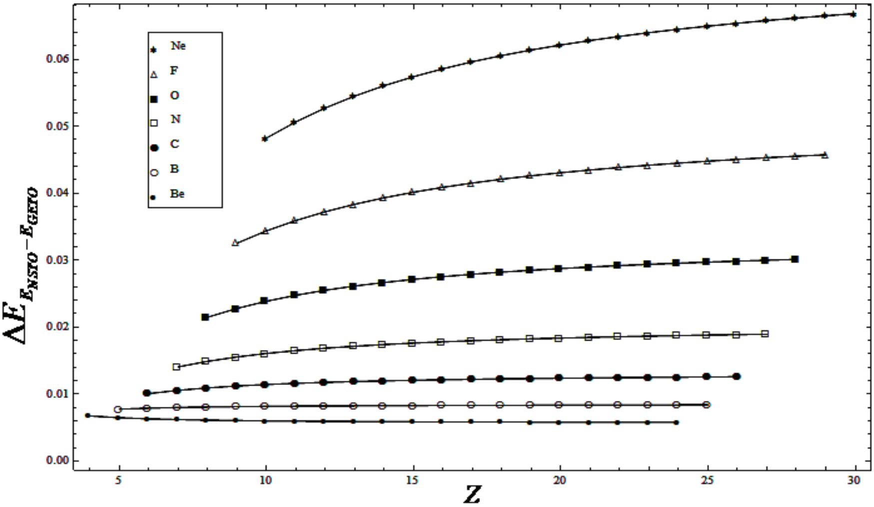

Fig. 2. The energy differences between E_{NSTO} and E_{GETO} as a function of atomic number Z for isoelectronic series of the atoms Be to Ne (in Hartree)

The CHFR total energy calculations have been also carried out for the ground states of isoelectronic series for the configurations K [Ar]4s^{0}3d^1 $\left({}^2D\right)$ and Cr$^+$ [Ar] 4s^{0}3d^5 $\left({}^6S\right)$. For these isoelectronic series, in tables 2 and 3, we present the total energies obtained from the GETO and NSTO basis sets, μ values and total energy differences between E_{GETO} and E_{NSTO} ($\Delta E_{E_{NSTO}-E_{NHF}}$ and $\Delta E_{E_{GETO}-E_{NHF}}$). As can be seen from these tables, the efficiency of NSTO and GETO basis sets in the total energy calculations for the isoelectronic series of configurations K [Ar]$4s^0 3d^1$ $({}^2D)$ and Cr^+ [Ar] $4s^0 3d^5$ $({}^6S)$ is poor when compared to the isoelectronic series for Be to Ne atoms. The $\Delta E_{E_{GETO}-E_{NHF}}$ values for these isoelectronic series decrease smoothly with an increase the atomic number Z. It should be noted that the trend of total energy errors $\Delta E_{E_{NSTO}-E_{NHF}}$ in the case of isoelectronic series K [Ar]$4s^0 3d^1$ $({}^2D)$ using the NSTO basis sets is almost constant. The values of $\Delta E_{E_{NSTO}-E_{GETO}}$ and the variations of optimal principal quantum number in isoelectronic series considered have the similar behaviour with the isoelectronic series for Be to Ne. We notice that the deviations from nominal values of principal quantum number are largest for 3d-orbital, i.e., $1.732394876 \le n_{3d}^* \le 2.565245353$.

Table 2. The total energies E_{NSTO} and E_{GETO}, μ parameters, total energy differences $\Delta E_{E_{NSTO}-E_{NHF}}$ and $\Delta E_{E_{GETO}-E_{NHF}}$ for the isoelectronic series K [Ar]$4s^0 3d^1$ ${}^2D$ (in Hartree)

Z	$-E_{NSTO}$ [19]	$-E_{GETO}$ (μ)	$\Delta E_{E_{NSTO}-E_{NHF}}$ [19]	$\Delta E_{E_{GETO}-E_{NHF}}$
19	598.851381634	598.911060360 (0.963682106)	0.224330086	0.164651360
20	676.252721310	676.314566540 (0.964821735)	0.245729330	0.183884100
21	758.849276755	758.912216305 (0.966148393)	0.243090535	0.180150985
22	846.509362081	846.572918564 (0.967473187)	0.240079999	0.176523516
23	939.207319355	939.271364871 (0.968711704)	0.238329075	0.174283559
24	1036.932938799	1036.997397943 (0.969871444)	0.237475601	0.173016457
25	1139.680087694	1139.744906532 (0.970912369)	0.237258916	0.172440078
26	1247.444559744	1247.509697014 (0.971954773)	0.237513546	0.172376276
27	1360.223277271	1360.288699316 (0.972878150)	0.238131829	0.172709784
28	1478.013899031	1478.079578125 (0.973746579)	0.239041079	0.173361985
29	1600.814595675	1600.880508682 (0.974586014)	0.240190505	0.174277498
30	1728.623908862	1728.690035887 (0.975368203)	0.241543508	0.175416483

Table 3. The total energies E_{NSTO} and E_{GETO}, μ parameters, total energy differences $\Delta E_{E_{NSTO}-E_{NHF}}$ and $\Delta E_{E_{GETO}-E_{NHF}}$ for the isoelectronic series Cr^+ [Ar] $4s^0 3d^5$ ^6S (in Hartree)

Z	$-E_{NSTO}$ [19]	$-E_{GETO}$ (μ)	$\Delta E_{E_{NSTO}-E_{NHF}}$ [19]	$\Delta E_{E_{GETO}-E_{NHF}}$
24	1042.636094901	1042.719267611 (0.965909687)	0.503298249	0.420125539
25	1148.633507128	1148.718702208 (0.966853037)	0.475713172	0.390518092
26	1260.156391428	1260.243290693 (0.967806264)	0.458585522	0.371686257
27	1377.181383800	1377.269759520 (0.968712856)	0.447476340	0.359100620
28	1499.694945177	1499.784619773 (0.969582764)	0.440109503	0.350434907
29	1627.688157939	1627.778987724 (0.970424026)	0.4352227210	0.344392936
30	1761.154680347	1761.246546239 (0.971229365)	0.432062473	0.340196581

We report in this study the results of CHFR calculations of electronic ground states for isoelectronic sequences of atomic ions. In particular, the efficiencies of the GETO and NSTO basis sets for isoelectronic series of atoms Be to Ne and, K and Cr^+ are investigated within the minimal basis sets approximation. The optimum μ values, which are always smaller than 1, are determined in GETO basis sets for ground states of all the isoelectronic series. It is found that the optimum n_{1s}^* values obtained are larger for GETO and smaller for NSTO basis sets than the nominal value 1. These results show that the GETO basis sets can be fulfilled the criteria which are the cusp value and asymptotic long-range behavior of orbitals.

We show that the efficiency of the GETO basis sets increase especially with increase the atomic number Z in isoelectronic series of light atoms. We notice that, for all of the isoelectronic series considered the orbital energies using GETO and NSTO are improved within the minimal basis sets framework. The resulting wave functions and parameters are available by request through e-mail addresses: ihuseyin@comu.edu.tr or merturk@comu.edu.tr

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