

On the effectiveness of exponential type orbitals with hyperbolic cosine functions in atomic calculations

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Abstract Unconventional basis functions, constructed from exponential type orbitals (ETOs) with hyperbolic cosine functions, are applied to Roothaan-Hartree-Fock calculations of atoms within the minimal basis sets framework. The most popular ETOs, Slater type orbitals, B functions and $\psi^{(\alpha^*)}$ functions with $\alpha^* = 2$, and two types of hyperbolic cosine functions, $\cosh(\beta r)$ and $\cosh(\beta r + \gamma)$, are used in this work. The performance of the present basis functions is investigated and compared to the conventional double-zeta Slater-type basis set and numerical Hartree-Fock results. The improvement in the atomic energies clearly demonstrates how the accuracy increases when we move from ETO to ETO with hyperbolic cosine basis functions. The resulting improved minimal basis sets can also be useful in molecular calculations.

Keywords Hyperbolic cosine function · Exponential type orbital · Roothaan-Hartree-Fock calculation

1 Introduction

It is well known that Roothaan-Hartree-Fock (RHF) approximation [1,2] is widely used in electronic structure calculations of atoms and molecules. Since the determination of the physical properties of atomic and molecular systems requires the use of reliable basis sets, the selection of appropriate basis functions is of fundamental

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importance for both the accuracy and computational cost. Exponential type orbitals (ETOs) describe correctly the asymptotic behaviour of the exact electronic wave function, namely, the cusps at the nuclei [3] and exponential decay at large distances [4]. Therefore, ETOs would be desirable as basis functions. Some of the ETOs receive much attention in RHF method because of their useful properties:

The Slater type orbitals with integer principal quantum number n (ISTOs) are the simplest and commonly used basis functions in atomic calculations [5–8] and are defined as [9, 10]

$$\chi_{nlm}(\zeta; \vec{r}) = \frac{(2\zeta)^{n+(1/2)}}{[(2n)!]^{1/2}} r^{n-1} e^{-\zeta r} S_{lm}(\theta, \varphi), \quad (1)$$

where $S_{lm}(\theta, \varphi)$ denotes complex or real spherical harmonic and ζ is the orbital exponent.

The B functions (BTOs) are also used in atomic and molecular calculations [11–13] due to their remarkably simple Fourier transforms and are given by [14]

$$B_{nlm}(\zeta; \vec{r}) = \frac{(\zeta r)^l}{2^{n+l}(n+l)!} \hat{k}_{n-1/2}(\zeta r) S_{lm}(\theta, \varphi), \quad (2)$$

where $\hat{k}_\nu(x)$ is the reduced Bessel function.

Alternative to these ETOs, the complete orthonormal sets of $\psi^{(\alpha^*)}$ functions introduced by Guseinov [15, 16] are defined as

$$\psi_{nlm}^{(\alpha^*)}(\zeta; \vec{r}) = \left[\frac{(2\zeta)^3 (n-l-1)!}{(2n)^{\alpha^*} \Gamma(q^*+1)} \right]^{\frac{1}{2}} e^{-x/2} x^l L_{n-l-1}^{(p^*)}(x) S_{lm}(\theta, \varphi), \quad (3)$$

where $L_q^p(x)$ and $\Gamma(x)$ are the generalized Laguerre polynomials and gamma function, respectively and $p = 2l + 2 - \alpha^*$, $q = n + l + 1 - \alpha^*$, $-\infty < \alpha^* < 3$, $x = 2\zeta r$. The $\psi^{(\alpha^*)}$ functions are a general form of the complete orthonormal sets of ETOs involving Laguerre polynomials such as Coulomb-Sturmian ($\alpha^* = 1$) and Lambda ($\alpha^* = 0$) functions, and have been applied to atomic self consistent field calculations within the minimal basis sets approximation [17].

Despite the aforementioned benefits of ETOs, their use in molecular calculations is restricted due to the difficulties in the evaluation of molecular integrals [18]. Therefore, the developments in the construction of economic and efficient basis sets of ETOs are important for their application to electronic structure-property studies. In this context, in the last few decades, hyperbolic cosine $\cosh(\beta r)$ (HC) and modified hyperbolic cosine $\cosh(\beta r + \gamma)$ (MHC) functions have been incorporated into non-integer n -Slater type orbitals (NISTOs). It has been reported that the NISTO with HC function (NISTO-HC) [19] and NISTO with MHC function (NISTO-MHC) [20] have provided remarkably improvement in atomic RHF energies within the minimal basis sets framework. Similarly, in recent works, the HC and MHC functions have also been combined with $\psi^{(\alpha^*)}$ functions [21] and generalized ETOs [22–24] in order to increase the basis set quality.

It should be noted that the use of HC and MHC functions splits exponential part of an ETO into equally and different-weighted two components, respectively:

$$e^{-\zeta r} \cosh(\beta r) = \frac{1}{2}(e^{-(\zeta+\beta)r} + e^{-(\zeta-\beta)r}), \quad (4)$$

$$e^{-\zeta r} \cosh(\beta r + \gamma) = \frac{1}{2}(e^{-\gamma} e^{-(\zeta+\beta)r} + e^{\gamma} e^{-(\zeta-\beta)r}). \quad (5)$$

Here ζ , β and γ are the variational parameters with a constraint $\zeta > \beta \geq 0$, γ can be either positive, zero or negative. Thus, ETO with HC type basis functions provide a double-zeta effect with a single basis function using fewer number of variational parameters.

The purpose of this paper is to combine HC and MHC functions with frequently used ETOs and compare the performances of ETO with HC type basis functions to each other using the same number of variational parameters. For this purpose, we use ISTO, BTO and $\psi^{(2)}$ functions (We select $\alpha^* = 2$ case for $\psi^{(\alpha^*)}$ functions because $\psi^{(2)}$ gives the best energy values for atoms among the $\psi^{(\alpha^*)}$ functions with fixed integer parameter α^* [17]). We define ETO-HC and ETO-MHC functions in this work as follows:

$$H_{nlm}^{\phi}(\zeta, \beta; \vec{r}) = N_{\phi}(\zeta, \beta) \phi_{nlm}(\zeta; \vec{r}) \cosh(\beta r), \quad (6)$$

$$M_{nlm}^{\phi}(\zeta, \beta, \gamma; \vec{r}) = N_{\phi}(\zeta, \beta, \gamma) \phi_{nlm}(\zeta; \vec{r}) \cosh(\beta r + \gamma), \quad (7)$$

where $N_{\phi}(\zeta, \beta)$ and $N_{\phi}(\zeta, \beta, \gamma)$ are the normalization constants depend on the chosen ETO. Using Eq. (6), one can construct BTO-HC, ISTO-HC and $\psi^{(2)}$ – HC functions for $\phi_{nlm}(\zeta; \vec{r}) = B_{nlm}(\zeta; \vec{r})$, $\phi_{nlm}(\zeta; \vec{r}) = \chi_{nlm}(\zeta; \vec{r})$ and $\phi_{nlm}(\zeta; \vec{r}) = \psi_{nlm}^{(2)}(\zeta; \vec{r})$, respectively. Analogously, BTO-MHC, ISTO-MHC and $\psi^{(2)}$ – MHC functions can be obtained from Eq. (7).

In order to demonstrate the efficiency of ETO-HC and ETO-MHC functions (ETO \equiv BTO, ISTO and $\psi^{(2)}$), we have performed RHF calculations with these functions for the ground states of some closed and open shell neutral atoms up to atomic number $Z = 20$. The computational method is described in the next section. Hartree atomic units are used throughout this work.

2 Computational method

All the one- and two-electron integrals required in this work were expressed by linear combinations of basic atomic integrals. The new integral package was incorporated into our atomic RHF program [17,25,26] which is written in Mathematica programming language [27]. The nonlinear parameters $\{\zeta, \beta, \gamma\}$ in basis functions were variationally optimized by using the methods exist in Mathematica programming language such as Newton, quasi-Newton, conjugate gradient and principal axis. To find the best minimum energy values and to avoid local minimums, we have performed optimization process several times using different starting points for all nonlinear

parameters and applying above mentioned methods. It should be noted that optimization process of Mg, Ar and Ca atoms with $\psi^{(2)} - \text{HC}$ functions could not be fully completed because total energies of these atoms depend on $\zeta - \beta$ differences of some basis functions and increase continuously with increasing ζ and β parameters. Therefore, in these cases, we imposed the restriction $0 \leq \beta < \zeta < 2Z$ which is the most suitable interval according to our analysis. It should be noted that we have not observed any simple relationship or regularity for the optimized nonlinear parameters ζ , β and γ of all the species examined.

For the reliable comparison of the results obtained with different basis functions, the conventional principal quantum numbers were used in atomic basis sets. In all our final wavefunctions, the virial ratios are in agreement to within seven decimal figures of the exact value (-2) and this indicates that our nonlinear optimizations are sufficiently accurate.

3 Results and discussion

By the use of ETO-HC and ETO-MHC basis functions (ETO \equiv BTO, ISTO and $\psi^{(2)}$), we have carried out RHF calculations for some atoms with atomic number $Z \leq 20$ within the minimal basis sets framework.

The ETO-HC and ETO-MHC energies are given in Table 1. The conventional double-zeta ISTO basis set (ISTO-CDZ) energies [28] are also tabulated in this table for comparative purposes. Among the ETO-HC functions, the $\psi^{(2)} - \text{HC}$ gives the best results for light atoms. However, as one moves to heavier atoms, the performance of the ISTO-HC basis sets is better than the others. We can easily see from Table 1 that the ETO-MHC energies remarkably lower than the ETO-HC ones for all the ETOs. This is because of additional variational parameter γ which removes the equally-weight restriction existing in the ETO-HC functions. The ETO-MHC results can also be compared with the ISTO-CDZ energies to show the accuracy of these basis functions. The $\psi^{(2)} - \text{MHC}$ basis sets for first row atoms give slightly more accurate energy values than their corresponding ISTO-CDZ basis sets. On the other hand, ISTO-MHC basis sets give closer results to ISTO-CDZ values than $\psi^{(2)} - \text{MHC}$ and BTO-MHC basis sets for remaining atoms. Thus, when we compare the ETO-MHC basis set qualities with each other, a similar trend is observed as in the case of ETO-HC results.

Figure 1 shows the energy errors (ΔE) of the ETO-HC and ETO-MHC basis sets, relative to the numerical Hartree–Fock (NHF) values [7]. We note that the error plots of $\psi^{(2)}$ - and ISTO-based basis sets are similar to those of their $\psi^{(\alpha^*)}$ - and NISTO-based analogues, respectively [19–21]. In general, the energy errors do not increase smoothly with an increasing atomic number Z . The ETO-HC error curves have a common peak at Ne ($Z = 10$). The maximum energy errors are found at Ne atom as 0.2346, 0.2327 and 0.2085 hartrees for BTO-HC, ISTO-HC and $\psi^{(2)} - \text{HC}$ basis sets, respectively. As can be seen from Fig. 1, the ETO-MHC basis sets remarkably reduce the energy errors. For example, the errors for Ne atom are reduced to 0.0227, 0.0414 and 0.0118 hartrees by BTO-MHC, ISTO-MHC and $\psi^{(2)} - \text{MHC}$ basis sets, respectively.

In order to compare the contributions of HC and MHC functions to parent ETOs in atomic energy calculations, the differences between the results of ETO and ETO-HC

Table 1 The ETO-HC, ETO-MHC (ETO \equiv BTO, ISTO and $\psi^{(2)}$) and ISTO-CDZ energies for the ground state of some neutral atoms (sign reversed, in a. u.)

Atom	E _{BTO} -HC	E _{ISTO} -HC	E $\psi^{(2)}$ -HC	E _{BTO} -MHC	E _{ISTO} -MHC	E $\psi^{(2)}$ -MHC	E _{ISTO} -CDZ ^a
He (¹ S)	2.86143320	2.86143320	2.86143320	2.86167263	2.86167263	2.86167263	2.86167263
Be (¹ S)	14.56663115	14.56834565	14.57203037	14.57207779	14.57020549	14.57296004	14.57237061
B (² P)	24.51747298	24.51978792	24.52595827	24.52708649	24.52346443	24.52868185	24.52792149
C (³ P)	37.66755966	37.67012925	37.67898293	37.68489011	37.67917801	37.68754723	37.68675127
N (⁴ S)	54.36308617	54.36567881	54.37756166	54.39457346	54.38638054	54.39869385	54.39795594
O (³ P)	74.72775901	74.73034225	74.74594885	74.79897677	74.78766709	74.80497127	74.80433335
F (² P)	99.26274274	99.26510923	99.28479613	99.39352737	99.37871117	99.40177895	99.40131911
Ne (¹ S)	128.31247584	128.31443285	128.33858965	128.52442813	128.50570438	128.53533904	128.53511980
Mg (¹ S)	199.44569173	199.45763444	199.50396502	199.59751158	199.60331746	199.60000450	199.60703454
Ar (¹ S)	526.69391102	526.69585236	526.64118319	526.74114753	526.79756618	526.74909918	526.81514489
Ca (¹ S)	676.62045906	676.65787662	676.61934457	676.66396711	676.74796339	676.70249189	676.75617159

^a The ISTO-CDZ energies were taken from [28]

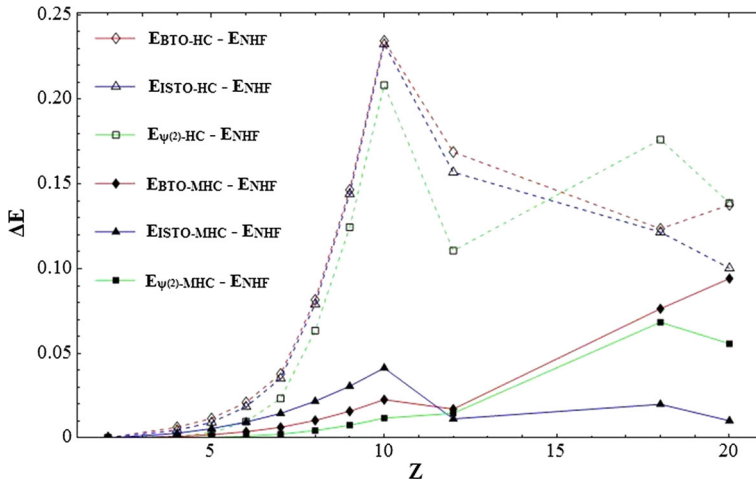


Fig. 1 The E_{ETO-HC} and $E_{ETO-MHC}$ energy errors ΔE relative to the E_{NHF} values (in a. u.).

Table 2 The energy differences of ETO-HC and ETO-MHC basis sets with respect to ETO (ETO \equiv BTO, ISTO and $\psi^{(2)}$) basis sets* ($\Delta E_X^{HC} = E_X - E_{X-HC}$ and $\Delta E_X^{MHC} = E_X - E_{X-MHC}$, in a. u.)

Atom	ΔE_{BTO}^{HC}	ΔE_{ISTO}^{HC}	$\Delta E_{\psi^{(2)}}^{HC}$	ΔE_{BTO}^{MHC}	ΔE_{ISTO}^{MHC}	$\Delta E_{\psi^{(2)}}^{MHC}$
He(1S)	0.01377695	0.01377695	0.01377695	0.01401638	0.01401638	0.01401638
Be(1S)	0.03152995	0.01160579	0.01998841	0.03697659	0.01346563	0.02091808
B(2P)	0.05111310	0.02141930	0.03510988	0.06072661	0.02509581	0.03783346
C(3P)	0.08854156	0.04774064	0.06892045	0.10587201	0.05678940	0.07748475
N(4S)	0.15011751	0.09677923	0.12746221	0.18160480	0.11748096	0.14859440
O(3P)	0.25839765	0.18997760	0.23087452	0.32961541	0.24730244	0.28989694
F(2P)	0.40790442	0.32299598	0.37613361	0.53868905	0.43659792	0.49311643
Ne(1S)	0.60508546	0.50225185	0.56962633	0.81703775	0.69352338	0.76637572
Mg(1S)	0.81222016	0.59984784	0.81412988	0.96404001	0.74553086	0.91016936
Ar(1S)	1.59161542	0.93059876	1.85233607	1.63885193	1.03231258	1.96025206
Ca(1S)	1.92526146	1.02398032	2.08810468	1.96876951	1.11406709	2.17125200

* The ISTO energies were taken from [5]. The BTO energies were taken from [11]. The $\psi^{(2)}$ energies were taken from [17]

basis sets, and the results of ETO and ETO-MHC basis sets are listed in Table 2. Addition of both HC and MHC functions significantly improve the basis function quality of all the ETOs examined in this work. Efficiency of the ETO-HC and ETO-MHC functions relative to the parent ETO increases with an increasing atomic number Z . We note from Table 2 that the energy differences between ETO and ETO-HC basis sets are larger than between ETO-HC and ETO-MHC basis sets. These results indicate that the parameter β has more effect than the parameter γ on the basis function quality. It is also seen that the accuracy improvement in the ISTO is smaller than the BTO

and $\psi^{(2)}$ function. This is contrary to the performances of the examined ETOs within the minimal basis framework. The ISTO gives better results in atomic calculations but incorporated HC and MHC functions bring closer the quality of these ETOs to each other.

Due to the fixed integer parameter $\alpha = 2$, the $\psi^{(2)}$ -HC and $\psi^{(2)}$ -MHC energies do not reach the $\psi^{(\alpha^*)}$ -HC and $\psi^{(\alpha^*)}$ -MHC ones [21], respectively. Similarly, ISTO-HC and ISTO-MHC yield higher energy values than NISTO-HC [19] and NISTO-MHC [20], respectively. The energy differences between ISTO- and NISTO-based basis sets are larger than between $\psi^{(2)}$ - and $\psi^{(\alpha^*)}$ -based basis sets. Because the parameter α^* in the $\psi^{(\alpha^*)}$ functions is common to all basis functions but n^* in the NISTOs is different for each basis function in an atom. For example, the energy differences (in hartree) for Ne atom are $0.000042(E_{\psi^{(2)}-HC} - E_{\psi^{(\alpha^*)-HC}})$, $0.000378(E_{\psi^{(2)}-MHC} - E_{\psi^{(\alpha^*)-MHC})}$, $0.133412(E_{ISTO-HC} - E_{NISTO-HC})$ and $0.0375(E_{ISTO-MHC} - E_{NISTO-MHC})$, respectively. It may be said that these differences are acceptable because we use fewer number of variational parameters. Moreover, the noninteger parameters α^* and n^* can restrict the applicability of such ETO with HC type basis functions to molecular calculations by causing additional time consuming difficulties in the molecular integral computations. For this reason, the present ETO-HC and ETO-MHC basis functions could be more convenient for molecular structure calculations.

4 Conclusion

We have applied ETO-HC and ETO-MHC type basis functions to atomic RHF calculations. The presented results clearly demonstrate how the accuracy is increased when we move from ETO via ETO-HC to ETO-MHC functions. It is shown that addition of HC and MHC function improves the performances of polynomial type functions (i.e., BTO and $\psi^{(2)}$) more than of ISTO within the minimal basis framework. Each type of the ETO-MHC function, and likewise the ETO-HC function, yields results of almost similar quality.

According to the above-mentioned statement, such improved minimal basis set descriptions of atoms could also be advantageous for the determination of various properties of molecules. Therefore, the proposed different basis functions can be chosen properly for atomic and molecular studies when RHF and semi-empirical molecular orbital methods are employed. All the present wavefunctions are available upon request to ES at the e-mail address: ercan.sahin@amasya.edu.tr.

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