Systematic Truncation of a Distributed Universal Even-Tempered Basis Set of Gaussian Functions: an Application to the Ground State of the BF Molecule

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Abstract

Systematic sequences of distributed universal even-tempered basis sets of Gaussian functions have been shown to support an accuracy approaching the sub-µHartree level for the total Hartree-Fock energies for diatomic molecules containing first row atoms. They have also been shown to support high precision correlation treatments. Furthermore, the use of a similar approach for systems containing heavy atoms and for polyatomic molecules has been demonstrated. In this paper, systematic truncation of basis sets developed in this fashion is explored. An application to the Hartree-Fock ground state of the BF molecule at its equilibrium geometry is described. The parent distributed universal basis set, which contains a total of 623 primitive Gaussian functions, is truncated by systematically removing those basis functions for which the magnitude of the elements of the orbital expansion coefficient vector are less than some small \( \tau \) for all occupied orbitals. The effects of truncation on the description of electron correlation effects using second order many-body perturbation theory is also explored.

1. Introduction

In this paper, the systematic truncation of a distributed universal even-tempered basis set capable of supporting high precision in both matrix Hartree-Fock and second order many-body perturbation theory calculations is explored using the ground state of the boron fluoride molecule as a prototype. The truncation procedure adopted is based on the magnitude of the orbital expansion coefficients associated with a given basis function in each of the occupied orbitals.

Finite basis set expansions are ubiquitous in \textit{ab initio} molecular electronic structure studies and are widely recognized as one of the major sources of error in contemporary calculations [1–5] . Since the pioneering work by Hartree and his co-workers in the 1930s, finite difference methods have been used in atomic Hartree-Fock calculations. It is only in the past fifteen years or so that finite difference techniques [6–10] (and more recently, finite element methods [11–14]) have been applied to the molecular Hartree-Fock problem. By exploiting spheroidal co-ordinates, two-dimensional Hartree-Fock calculations for diatomic molecules have become possible. These calculations have provided benchmarks which, in turn, have enabled the finite basis set approach to be refined to the point where matrix Hartree-Fock calculations for diatomic molecules can yield energies which approach the µ-Hartree level of accuracy [15–18]. Furthermore, these basis sets can then be employed in calculations for polyatomic molecules [19,20] which are not, at present, amenable to finite difference or finite element techniques.
Finite basis set Hartree-Fock calculations yield not only an approximation for the occupied orbitals but also a representation of the spectrum which can be used in the treatment of correlation effects. In particular, the use of finite basis sets facilitates the effective evaluation of the sum-over-states which arise in the many-body perturbation theory of electron correlation effects in atoms and molecules. Basis sets have been developed for low order many-body perturbation theoretic treatments of the correlation problem which yield electron correlation energy components approaching the sub-milliHartree level of accuracy [20,21,22].

The truncation procedure explored in the present study is described in detail in section 2. An analysis of the orbital expansion coefficients for the ground state of the BF molecule is presented in section 3, where the truncated basis sets employed in the present study are defined. The results of both matrix Hartree-Fock calculations and second-order many-body perturbation theory studies are given in section 4 together with a discussion of the properties of the truncated basis sets. The final section, section 5, contains a discussion of the results and conclusions are given.

### 2. Truncation of a Distributed Universal Even-tempered Basis Set

In our previous work [23], we have investigated the use of distributed basis sets for molecular electronic structure calculations; that is, basis sets which comprise a number of subsets; each subset being centred on a different point in space. In approaching the Hartree-Fock limit, we have found that in addition to the usual atom-centred subsets, functions centred on the bond mid-point are also very useful. For the ground state of the boron fluoride molecule, which we use as a prototype in the present study, such a basis sets may be designated

$$S = S_B \oplus S_F \oplus S_{bc}$$  \hspace{1cm} (1)

where $S_B$ and $S_F$ denotes subsets centred on the boron and fluorine nuclei, respectively, and $S_{bc}$ represents a subset centred on the mid-point of the bond. Each of the subsets on a particular centre may be further decomposed into different symmetry types: s, p, d, f, …

$$S_X = S_X(s) \oplus S_X(p) \oplus S_X(d) \oplus \ldots, X = B, F, bc$$  \hspace{1cm} (2)

In the present work, the highest symmetry type included on the atomic centres are $f$-type functions, whilst on the bond centre symmetries up to and including $d$ are employed.

In our previous work [15–22], we have used a universal sequence of distributed even-tempered basis set in which the exponents for each symmetry type form a geometric series according to the formula $\zeta_k = \alpha \beta^k$ on each expansion centre. Different parameters $\alpha$ and $\beta$ were used for the functions of $s$-type in order to provide the additional flexibility required to obtain a satisfactory description of any cusp at the point upon which the functions were centred. Common values of $\alpha$ and $\beta$ were used for $p$-type functions and functions of higher symmetry. The orbitals, both occupied and unoccupied, are then approximated by an expansion of the form