Numerical Methods for Solving the Hartree-Fock Equations of Diatomic Molecules I

John C. Morrison[1,*], Scott Boyd[1], Luis Marsano[1], Bernard Bialecki[2], Thomas Ericsson[3] and Jose Paulo Santos[4]

[1] *Department of Physics, University of Louisville, Louisville, KY, 40292, USA.*
[2] *Department of Mathematical and Computer Sciences, Colorado School of Mines, Golden, CO 80401-1887, USA.*
[3] *Department of Mathematical Sciences, Chalmers University of Technology and the University of Gothenburg, SE-412 96 Gothenburg, Sweden.*
[4] *Department of Physics, New University of Lisbon, Lisbon, Portugal.*

Abstract. The theory of domain decomposition is described and used to divide the variable domain of a diatomic molecule into separate regions which are solved independently. This approach makes it possible to use fast Krylov methods in the broad interior of the region while using explicit methods such as Gaussian elimination on the boundaries. As is demonstrated by solving a number of model problems, these methods enable one to obtain solutions of the relevant partial differential equations and eigenvalue equations accurate to six significant figures with a small amount of computational time. Since the numerical approach described in this article decomposes the variable space into separate regions where the equations are solved independently, our approach is very well-suited to parallel computing and offers the long term possibility of studying complex molecules by dividing them into smaller fragments that are calculated separately.

1 Introduction

The solution of the multiconfiguration Hartree-Fock equations (MCHF) provide an approximate description of atoms and molecules and serve as the starting point of more

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*Corresponding author. *Email addresses:* `johnc@erdos.math.louisville.edu` (J. C. Morrison), `bbialeck@mines.edu` (B. Bialecki), `thomas@math.chalmers.se` (T. Ericsson), `jps@fct.unl.pt` (J. P. Santos)

accurate calculations. Accurate numerical solutions of the MCHF equations for atoms have been reported by Charlotte Froese Fisher [1,2]. Numerical solutions of the Hartree-Fock equations for diatomic molecules have been reported by E.A. McCullough Jr [3] and by Laaksonen and his collaborators [4,5]. More recently, we have reported numerical calculations using the spline collocation method which makes it possible to treat continuum as well as bound states [6,7]. While most researchers in theoretical chemistry would acknowledge that numerical methods can be very accurate, numerical calculations do not presently have the same range and flexibility as basis set work and are still not widely used.

The recent appearance of domain decomposition theories makes it possible to divide the variable domain into separate regions where molecular equations are solved independently. For diatomic molecules, the domain decomposition approach enables one to use fast Krylov methods in the broad interior of the physical region while using explicit methods such as Gaussian elimination on the boundaries. Such an approach has the capability of producing numerical results much more accurately and much more quickly than is currently possible. More generally, domain decomposition methods make it possible to calculate the properties of complex molecules by dividing them into smaller fragments.

Applications of the domain decomposition technique have been published for a number of years within the framework of the finite element method [8]. More recently, a domain decomposition theory for orthogonal spline collocation has been developed [9]. The calculations reported in this paper take advantage of the spline collocation formulation of the theory.

To begin solving the Hartree-Fock equations one typically makes an initial estimate of the wave functions and uses these wave functions to calculate the contributions of each pair of orbitals to the potential energy terms in the Hartree-Fock equations. The contributions due to the direct- and exchange-parts of the Coulomb interactions can be found by solving Poisson-like equations. The Hartree-Fock equations themselves are eigenvalue equations that may be solved to obtain new orbitals, and the entire process continued until self-consistency is achieved.

This article, which is denoted by the Roman letter I, will describe methods for solving the partial differential equations and eigenvalue equations that arise in the Hartree-Fock theory of diatomic molecules. The model problems we will solve in this article involve a single electron. A subsequent article denoted by the Roman letter II will discuss the solution of Poison-like equations and applies this theory to atoms and molecules having several electrons.

In Section 2 of this article, we shall show how the Hartee-Fock equations for diatomic molecules can be cast into self-adjoint forms that can be solved using Krylov methods. The self-adjoint equations all have the common property that they are singular on the boundary of the physical region. Section 3 shows how molecular wave functions can be represented by Hermite splines. Much of this material on splines has appeared before [6,7] but is include here for completeness. The domain decomposition theory described in Section 4 enables one to divide the entire region into separate domains in which the