

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

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**Abstract.** In order to solve the partial differential equations that arise in the Hartree-Fock theory for diatomic molecules and in molecular theories that include electron correlation, one needs efficient methods for solving partial differential equations. In this article, we present numerical results for a two-variable model problem of the kind that arises when one solves the Hartree-Fock equations for a diatomic molecule. We compare results obtained using the spline collocation and domain decomposition methods with third-order Hermite splines to results obtained using the more-established finite difference approximation and the successive over-relaxation method. The theory of domain decomposition presented earlier is extended to treat regions that are divided into an arbitrary number of subregions by families of lines parallel to the two coordinate axes. While the domain decomposition method and the finite difference approach both yield results at the micro-Hartree level, the finite difference approach with a 9-point difference formula produces the same level of accuracy with fewer points. The domain decomposition method has the strength that it can be applied to problems with a large number of grid points. The time required to solve a partial differential equation for a fine grid with a large number of points goes down as the number of partitions increases. The reason for this is that the length of time necessary for solving a set of linear equations in each subregion is very much dependent upon the number of equations. Even though a finer partition of the region has more subregions, the time for solving the set of linear equations in each subregion is very much smaller. This feature of the theory may well prove to be a decisive factor for solving the two-electron pair equation, which – for a diatomic molecule – involves solving partial differential equations with five independent variables. The domain decomposition theory also makes it possible to study complex molecules by dividing them into smaller fragments that

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are calculated independently. Since the domain decomposition approach makes it possible to decompose the variable space into separate regions in which the equations are solved independently, this approach is well-suited to parallel computing.

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**Key words:** Pair equation, Hartree-Fock equation, domain decomposition, Hermite splines, high-order finite differences, successive over-relaxation.

## 1 Introduction

The multiconfiguration Hartree-Fock equations (MCHF) provide an approximate description of atoms and molecules and serve as the starting point of more accurate calculations. Accurate numerical solutions of these equations for atoms have been reported by Fisher [1, 2]. Numerical solutions of the Hartree-Fock equations for diatomic molecules have been reported by McCullough [3], Heinemann and coworkers [4, 5] and Laaksonen, Pykkö, and Sundholm [6], and more recently by Kobus, Laaksonen, and Sundholm [7, 8].

The first article of this series [9] shows how the spline collocation and domain decomposition methods can be used to solve Poisson-like equations in two variables. This was a necessary step for solving the Hartree-Fock equations for diatomic molecules since the HF equations themselves are of the same form as the Poisson equation and the Coulomb and exchange potentials in the HF equations can be obtained by solving appropriate Poisson equations. The theory of domain decomposition presented earlier is extended to treat regions that are divided into an arbitrary number of subregions by vertical and horizontal interfaces. We test the approach by solving the equation for the  $\text{He}^+$  system and compare the results with the numerical ones using finite differences.

In Section 2 of this article, we shall give the Hartree-Fock equations for a diatomic molecule in spheroidal coordinates. Section 3 introduces the domain decomposition algorithm and applies the algorithm to a model problem in which a region is divided into an arbitrary number of subregions by families of lines parallel to the two coordinate axes. Section 4 shows how the eigenvalues and eigenfunctions of the Hartree-Fock theory can be obtained using the inverse iteration and the inverse Arnoldi method or, within the framework of finite differences, by using the Raleigh quotient. In this section we shall also compare results obtained using spline collocation and domain decomposition with results obtained using finite differences and the successive over-relaxation (SOR) method.

## 2 The Hartree-Fock equations for a diatomic molecule

The Hartree-Fock equations for a diatomic molecule in atomic units can be written (cf. [9])

$$\left[ -\frac{1}{2}\nabla^2 - \frac{Z_A}{r_A} - \frac{Z_B}{r_B} + \sum_b (2J_b - K_b) \right] \psi_a(\mathbf{r}) = \epsilon \psi_a(\mathbf{r}), \quad (2.1)$$