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

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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.

AMS subject classifications: 65N35, 65N22, 65F10

Key words: Fast Krylov methods, splines, Hartree-Fock equations, diatomic molecules, eigenvalue problem.

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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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

Hartree-Fock equations can be solved independently. The material in this section, which is entirely new, makes it possible for us to use the preconditioned conjugate gradient method in the broad interior of the physical region while using a banded Gaussian solver on the boundary. As we shall demonstrate by solving a number of model problems, these methods enable one to obtain wave functions accurate to six significant figures with a modest amount of computational time. Section 5 of this article shows how the domain decomposition theory may be used to solve eigenvalue problems.

2 Self-adjoint forms of the Hartree-Fock equations

The Hartree-Fock equation for a diatomic molecule in atomic units can be written

$$\left[-\frac{1}{2}\nabla^2-\frac{Z_a}{r_a}-\frac{Z_b}{r_b}+\sum_b(2J_b-K_b)\right]\psi(\mathbf{r})=\epsilon\psi(\mathbf{r}), \tag{2.1}$$

where r_a and r_b denote the distances of the electron from the two nuclei. The Coulomb interaction among the electrons is described by the direct and exchange functions J_b and K_b, which are defined by the equations

$$J_b\psi_a(\mathbf{r}_1)=\int\psi_b^*(\mathbf{r}_2)\frac{1}{r_{12}}\psi_b(\mathbf{r}_2)dV_2\cdot\psi_a(\mathbf{r}_1), \tag{2.2}$$

$$K_b\psi_a(\mathbf{r}_1)=\int\psi_b^*(\mathbf{r}_2)\frac{1}{r_{12}}\psi_a(\mathbf{r}_2)dV_2\cdot\psi_b(\mathbf{r}_1). \tag{2.3}$$

The positions of the nuclei and the electron are illustrated in Fig. 1. The distance between the two nuclei is denoted by R, and, as before, r_a and r_b denote the distances of the electron from the nuclei.

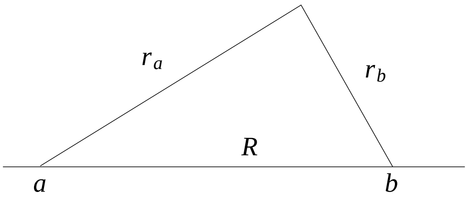

Figure 1: Positions of the nuclei and electron.

Diatomic molecules are usually described in spheroidal coordinates

$$\begin{aligned}&\xi=(r_a+r_b)/R, && \text{where } 1\le\xi<\infty,\\ &\eta=(r_a-r_b)/R, && \text{where } -1\le\eta\le1,\\ &\phi=\phi, && \text{where } 0\le\phi\le2\pi,\end{aligned} \tag{2.4}$$

in which the Laplacian operator assumes the form

$$\nabla^2=\frac{4}{R^2(\xi^2-\eta^2)}\left[\frac{\partial}{\partial\xi}(\xi^2-1)\frac{\partial}{\partial\xi}+\frac{\partial}{\partial\eta}(1-\eta^2)\frac{\partial}{\partial\eta}+\left(\frac{1}{\xi^2-1}+\frac{1}{1-\eta^2}\right)\frac{\partial^2}{\partial\phi^2}\right], \tag{2.5}$$

and the potential energy of the electron in the field of the two nuclei is

$$\frac{Z_a}{r_a}+\frac{Z_b}{r_b}=\frac{2}{R^2(\xi^2-\eta^2)}[R(Z_a+Z_b)\xi-R(Z_a-Z_b)\eta]. \tag{2.6}$$

This last equation may be written more compactly if one uses the special symbols, Z and Δ, to represent the sum and difference of the two nuclear charges. The potential energy due to the two nuclei then becomes

$$\frac{Z_a}{r_a}+\frac{Z_b}{r_b}=\frac{2}{R^2(\xi^2-\eta^2)}(RZ\xi-R\Delta\eta), \tag{2.7}$$

where $Z=Z_a+Z_b$ and $\Delta=Z_a-Z_b$. If one assumes that the single-electron wave function is of the general form

$$\psi(\xi,\eta,\phi)=\frac{e^{im\phi}}{(2\pi)^{1/2}}u(\xi,\eta), \tag{2.8}$$

the Hartree-Fock equations (2.1) can be written

$$\begin{aligned}&-\frac{\partial}{\partial\xi}(\xi^2-1)\frac{\partial u}{\partial\xi}-\frac{\partial}{\partial\eta}(1-\eta^2)\frac{\partial u}{\partial\eta}+\left(\frac{m^2}{\xi^2-1}+\frac{m^2}{1-\eta^2}\right)u\\&\quad+\left[-RZ\xi+R\Delta\eta+\frac{R^2}{2}(\xi^2-\eta^2)\sum_b(2J_b-K_b)\right]u=\frac{R^2}{2}(\xi^2-\eta^2)\epsilon u,\end{aligned} \tag{2.9}$$

where $Z=Z_a+Z_b$ and $\Delta=Z_a-Z_b$.

One can ensure that the grid points are clustered near the nuclei where the wave functions oscillate most rapidly by making a variable substitution. Following Laaksonen and his collaborators [5], we make the transformations

$$\begin{aligned}\eta&=\cos\nu \quad &&\text{for } 0\le\nu\le\pi,\\ \xi&=\cosh\mu \quad &&\text{for } 0\le\mu\le\infty.\end{aligned} \tag{2.10}$$

The Hartree-Fock equation then becomes

$$\begin{aligned}&\left[-\frac{\partial^2}{\partial\nu^2}-\left(\frac{\cos\nu}{\sin\nu}\right)\frac{\partial}{\partial\nu}-\frac{\partial^2}{\partial\mu^2}-\left(\frac{\cosh\mu}{\sinh\mu}\right)\frac{\partial}{\partial\mu}\right]u+\left(\frac{m^2}{\xi^2-1}+\frac{m^2}{1-\eta^2}\right)u\\&\quad+\left[-RZ\xi+R\Delta\eta+\frac{R^2}{2}(\xi^2-\eta^2)\sum_b(2J_b-K_b)\right]u=\frac{R^2}{2}(\xi^2-\eta^2)\epsilon u.\end{aligned} \tag{2.11}$$

and the wave function u satisfies homogeneous Neumann boundary conditions with respect to the new variables

$$\frac{\partial u}{\partial\nu}=\frac{\partial u}{\partial\eta}\frac{\partial\eta}{\partial\nu}=-\sin\nu\frac{\partial u}{\partial\eta}=0 \quad \text{for } \nu=0 \text{ or } \nu=\pi, \tag{2.12}$$

$$\frac{\partial u}{\partial \mu}=\frac{\partial u}{\partial \xi}\frac{\partial \xi}{\partial \mu}=\sinh\mu\frac{\partial u}{\partial \xi}=0 \qquad \text{for } \mu=0. \tag{2.13}$$

While the operator on the left-hand side of Eq. (2.11) is not self-adjoint, the operator can be made self-adjoint by multiplying the equation by the function $\sin\nu\sinh\mu$ to obtain

$$\begin{aligned}&-\sin\nu\sinh\mu\frac{\partial^2 u}{\partial \nu^2}-\cos\nu\sinh\mu\frac{\partial u}{\partial \nu}-\sin\nu\sinh\mu\frac{\partial^2 u}{\partial \mu^2}-\sin\nu\cosh\mu\frac{\partial u}{\partial \mu}\\&+\sin\nu\sinh\mu\left(\frac{m^2}{\xi^2-1}+\frac{m^2}{1-\eta^2}\right)u+\sin\nu\sinh\mu\Big[-RZ\xi+R\Delta\eta\\&+\frac{R^2}{2}(\xi^2-\eta^2)\sum_b(2J_b-K_b)\Big]u=\sin\nu\sinh\mu\frac{R^2}{2}(\xi^2-\eta^2)\epsilon u.\end{aligned} \tag{2.14}$$

Since the coefficient of each first derivative in the above equation is equal to the derivative of the corresponding second derivative and since the function u satisfies homogeneous Neumann boundary equations, the differential operator on the left-hand side of Eq. (2.14) is self-adjoint.

The function $\cosh\mu$ appearing in the second transformation equation (2.10) has an exponential dependence for long distances and is hence well-suited for bound solutions. For free-electron states, a square root transformation of the coordinates is more appropriate. We thus define the transformation equations,

$$\begin{aligned}&\eta=\cos\nu &&\text{for } 0\le\nu\le\pi,\\&\xi=\mu^2+1 &&\text{for } 0\le\mu\le\infty.\end{aligned} \tag{2.15}$$

This transformation is suitable for free-electrons since the distance between adjacent grid points does not become too large far from the nuclei.

The Hartree-Fock equation obtained using the coordinate transformation (2.15) is

$$\begin{aligned}&\left[-\frac{\partial^2}{\partial \nu^2}-\left(\frac{\cos\nu}{\sin\nu}\right)\frac{\partial}{\partial \nu}-\frac{1}{4}(\mu^2+2)\frac{\partial^2}{\partial \mu^2}-\frac{1}{4\mu}(3\mu^2+2)\frac{\partial}{\partial \mu}\right]u+\left(\frac{m^2}{\xi^2-1}+\frac{m^2}{1-\eta^2}\right)u\\&+\left[-RZ\xi+R\Delta\eta+\frac{R^2}{2}(\xi^2-\eta^2)\sum_b(2J_b-K_b)\right]u=\frac{R^2}{2}(\xi^2-\eta^2)\epsilon u.\end{aligned} \tag{2.16}$$

The differential operator on the left-hand side of this last equation can be made self-adjoint by multiplying the equation by $\mu\sin\nu$.

The various forms of the Hartree-Fock equations we have considered thus far all have solutions that satisfy homogeneous Neumann boundary conditions. A Dirichlet form of the theory can be obtained by making the dependent variable transformation

$$v(\nu,\mu)=\sin\nu\sinh\mu\, u(\nu,\mu), \tag{2.17}$$

which forces the new function v to be zero on the boundary. The independent variable transformation (2.10) together with the dependent variable transformation (2.17) lead to the Hartree-Fock equations

$$\begin{aligned}&\left[-\frac{\partial^2}{\partial\nu^2}+\left(\frac{\cos\nu}{\sin\nu}\right)\frac{\partial}{\partial\nu}-\frac{\partial^2}{\partial\mu^2}+\left(\frac{\cosh\mu}{\sinh\mu}\right)\frac{\partial}{\partial\mu}\right]v+\left(\frac{m^2}{\xi^2-1}+\frac{m^2}{1-\eta^2}\right)v\\ &\qquad+\left[-\sin^{-2}\nu-\sinh^{-2}\mu-RZ\xi+R\Delta\eta+\frac{R^2}{2}(\xi^2-\eta^2)\sum_b(2J_b-K_b)\right]v\\ &=\frac{R^2}{2}(\xi^2-\eta^2)\epsilon v, \qquad (2.18)\end{aligned}$$

which can be made self-adjoint by multiplying by the factor $\sin^{-1}\nu\sinh^{-1}\mu$.

We have shown previously [7] that the coordinate transformation (2.10) together with the variable substitution,

$$v(\nu,\mu)=\sin^{1/2}\nu\sinh^{1/2}\mu\, u(\nu,\mu), \qquad (2.19)$$

leads to the self-adjoint equation

$$\begin{aligned}&-\frac{\partial^2 v}{\partial\nu^2}-\frac{\partial^2 v}{\partial\mu^2}+\left(\frac{m^2}{\xi^2-1}+\frac{m^2}{1-\eta^2}\right)v+\left[\frac{(\eta^2-2)}{4(1-\eta^2)}+\frac{(\xi^2-2)}{4(\xi^2-1)}\right.\\ &\qquad\left.-RZ\xi+R\Delta\eta+\frac{R^2}{2}(\xi^2-\eta^2)\sum_b(2J_b-K_b)\right]v=\frac{R^2}{2}(\xi^2-\eta^2)\epsilon v. \qquad (2.20)\end{aligned}$$

Each of the self-adjoint equations we have obtained in this section lead to difficulties on the boundary of the physical region. The coefficients of the derivatives in Eqs. (2.14) go to zero on the boundaries. Consequently, the differential operator on the left-hand side of the equation is not positive definite, and the efficient preconditioned conjugate gradient method may not be used to solve the linear system of equations that arise when the differential operator is discretized. The coefficients of the derivatives in the self-adjoint form of Eq. (2.18) and the first derivatives of the function v defined by Eq. (2.19) become infinite on the boundary.

All of the difficulties we have mentioned can be overcome by using the domain decomposition theory described in Section 4. The equations in the boundary region can be solved by an explicit method that does not depend upon the matrix being positive definite, and the preconditioned conjugate gradient method can be used in the broad interior of the physical regions where the coefficients of the derivatives of the partial differential equation are bounded away from zero.

3 Splines and differential equations

For solving partial differential equations, we shall use a continuous differentiable basis of fourth-order Hermite splines. To define the spline basis for a single variable x in the range, $a \le x \le b$, we define a partition of the interval, $x_i = a + ih$ where h is the step size and $i = 0,1,\cdots,N$. The points x_i are called *nodes*.

The basis functions $v_i(x)$ and $s_i(x)$ for $1 \le i \le N-1$ are defined by the equations

$$v_i(x) = \begin{cases} \frac{1}{h^3}(x-x_{i-1})^2[h+2(x_i-x)], & x_{i-1} \le x \le x_i, \\ \frac{1}{h^3}(x_{i+1}-x)^2[h+2(x-x_i)], & x_i \le x \le x_{i+1}, \\ 0, & \text{otherwise}, \end{cases} \tag{3.1}$$

$$s_i(x) = \begin{cases} \frac{1}{h^3}(x-x_{i-1})^2(x-x_i), & x_{i-1} \le x \le x_i, \\ \frac{1}{h^3}(x_{i+1}-x)^2(x-x_i), & x_i \le x \le x_{i+1}, \\ 0, & \text{otherwise}. \end{cases} \tag{3.2}$$

The values of these functions and their first derivatives at the nodal points follow immediately from Eqs. (3.1) and (3.2)

$$v_i(x_j) = \delta_{ij}, \quad v_i'(x_j) = 0, \quad s_i(x_j) = 0, \quad s_i'(x_j) = \delta_{ij}\frac{1}{h}, \tag{3.3}$$

where δ_{ij} is the Kronecker delta function. These conditions are sufficient to determine the polynomials within each interval.

The basis functions for the first and last intervals require special definitions

$$v_0(x) = \begin{cases} \frac{1}{h^3}(x-x_0)^2[h+2(x-x_0)], & x_0 \le x \le x_1, \\ 0, & \text{otherwise}, \end{cases} \tag{3.4}$$

$$s_0(x) = \begin{cases} \frac{1}{h^3}(x_1-x)^2(x-x_0), & x_0 \le x \le x_1, \\ 0, & \text{otherwise}, \end{cases} \tag{3.5}$$

$$v_N(x) = \begin{cases} \frac{1}{h^3}(x-x_{N-1})^2[h+2(x_N-x)], & x_{N-1} \le x \le x_N, \\ 0, & \text{otherwise}, \end{cases} \tag{3.6}$$

$$s_N(x) = \begin{cases} \frac{1}{h^3}(x-x_{N-1})^2(x-x_N), & x_{N-1} \le x \le x_N, \\ 0, & \text{otherwise}. \end{cases} \tag{3.7}$$

At $x_0 = a$, v_0 is equal to one and the derivative of s_0 is equal to $1/h$, while v_N is equal to one and the derivative of s_N is equal to $1/h$ at $x_N = b$. The functions v_i and s_i for $1 \le i \le N-1$, and the special functions v_0, s_0, v_N and s_N are illustrated in Fig. 2.

In this article, we shall describe the orthogonal spline collocation method for solving boundary value problems. The collocation method is most easily illustrated by solving

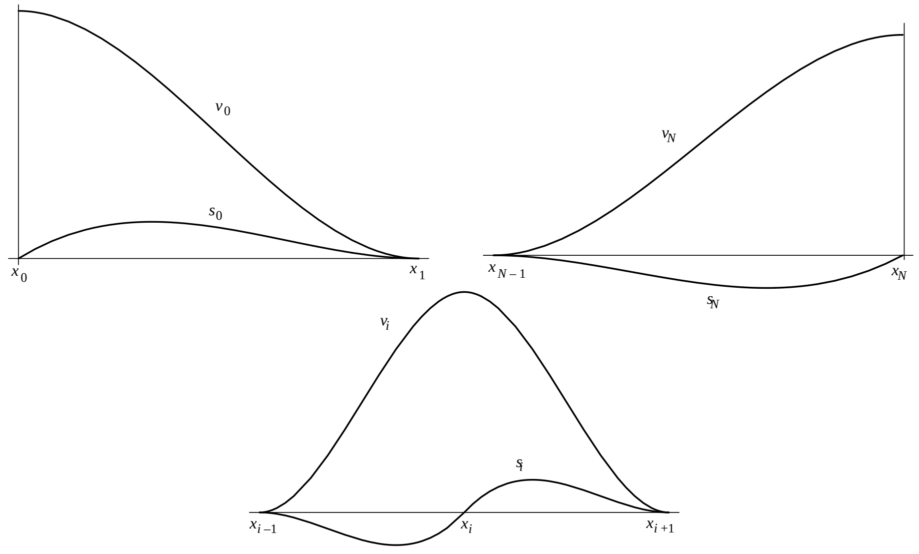

Figure 2: These three graphs show v_0, s_0, v_N, s_N and v_i,s_i, $1 \le i \le N-1$ (bottom).

an ordinary differential equation for a function of a single variable. The solution of an ordinary differential equation can be expressed as a linear combination of Hermite splines

$$u(x) = \sum_{i=0}^{N} [\alpha_i v_i(x) + \beta_i s_i(x)]. \tag{3.8}$$

For the Gauss quadrature points, ξ_{i1} and ξ_{i2}, within the i-th interval, four functions of the basis, v_{i-1}, s_{i-1}, v_i and s_i, have nonzero values. These functions are illustrated in Fig. 3. The Gauss points for cubic polynomials are given by the formulas

$$\xi_{i1} = x_{i-1} + \frac{3-\sqrt{3}}{6}h, \qquad \xi_{i2} = x_{i-1} + \frac{3+\sqrt{3}}{6}h. \tag{3.9}$$

Using (3.8), the solution can be evaluated at the Gauss points. We have

$$u(\xi_{i1}) = b_{11}\alpha_{i-1} + b_{12}\beta_{i-1} + b_{13}\alpha_i + b_{14}\beta_i, \tag{3.10}$$

$$u(\xi_{i2}) = b_{21}\alpha_{i-1} + b_{22}\beta_{i-1} + b_{23}\alpha_i + b_{24}\beta_i. \tag{3.11}$$

The coefficient matrix b_{ij} can be evaluated using Eqs. (3.1) and (3.2) and Eqs. (3.4)-(3.7). Eqs. (3.10) and (3.11) can be written in matrix form as

$$\begin{bmatrix} u(\xi_{i1}) \\ u(\xi_{i2}) \end{bmatrix} = \begin{bmatrix} b_{11} & b_{12} & b_{13} & b_{14} \\ b_{21} & b_{22} & b_{23} & b_{24} \end{bmatrix} \begin{bmatrix} \alpha_{i-1} \\ \beta_{i-1} \\ \alpha_i \\ \beta_i \end{bmatrix}. \tag{3.12}$$

Treating each of the subintervals in a similar manner, the vector $\mathbf{u_G}$ consisting of the values of the approximate solution at the Gauss points can be written as the product of a matrix times a vector

$$\mathbf{u_G} = \mathbf{B}\mathbf{u}, \tag{3.13}$$

where

$$\mathbf{u} = [\alpha_0, \beta_0, \alpha_1, \beta_1, \cdots, \alpha_N, \beta_N]^T, \tag{3.14}$$

$$\mathbf{u_G} = [u(\xi_{11}), u(\xi_{12}), u(\xi_{21}), u(\xi_{22}), \cdots, u(\xi_{N1}), u(\xi_{N2})]^T, \tag{3.15}$$

and $\mathbf{B}$ is a rectangular matrix having $2N+2$ columns and $2N$ rows. $\mathbf{B}$ has the structure

$$\mathbf{B} = \begin{bmatrix} \boxed{\mathbf{B}_1} & & & & \\ & \boxed{\mathbf{B}_2} & & & \\ & & \ddots & & \\ & & & \boxed{\mathbf{B}_{N-1}} & \\ & & & & \boxed{\mathbf{B}_N} \end{bmatrix}. \tag{3.16}$$

Two adjacent blocks $\mathbf{B}_i$ and $\mathbf{B}_{i+1}$ overlap in two columns.

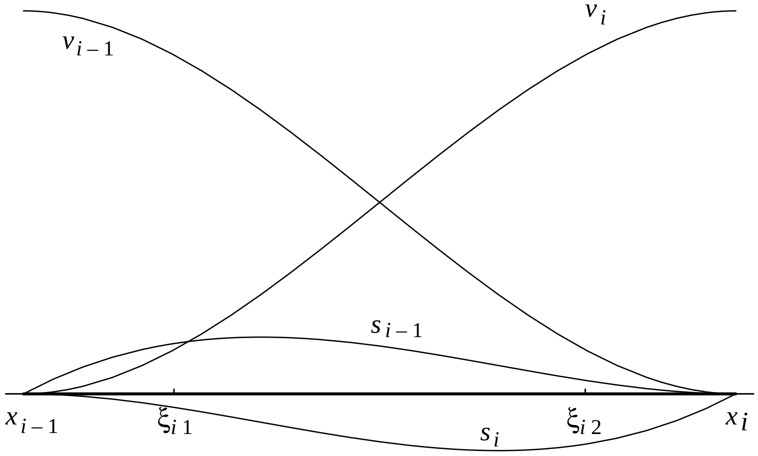

Figure 3: Four of the splines are nonzero at the Gauss points within the interval $[x_{i-1}, x_i]$.

The first and second derivatives of the approximate solution can be represented by matrices with the same block structure. We express the vector $\mathbf{u'_G}$ consisting of the values of the first derivative of the solution at the Gauss points as

$$\mathbf{u'_G} = \mathbf{C}\mathbf{u}, \tag{3.17}$$

where $\mathbf{u}$ is given by Eq. (3.14) and

$$\mathbf{u'_G} = [u'(\xi_{11}), u'(\xi_{12}), u'(\xi_{21}), u'(\xi_{22}), \cdots, u'(\xi_{N1}), u'(\xi_{N2})]^T. \tag{3.18}$$

The negative of the second derivative of the function at the Gauss points can be written

$$-\mathbf{u}''_{\mathrm{G}}=\mathbf{A}\mathbf{u}. \tag{3.19}$$

As for the matrix **B**, matrices **C** and **A** have $N+2$ columns and $2N$ rows, and the Hamiltonian of the system will have this property. The matrices may be converted into square matrices by adding a single row to the top and bottom of these matrices. These additional rows may be chosen to impose the boundary conditions. In the case of homogenous Dirichlet or Neumann boundary conditions, the boundary conditions can also be imposed by removing from the matrices **B**, **C**, and **A** the columns corresponding to the zero value of the functions or its derivatives. The matrices then have the same number of rows and columns.

We now use the spline representation of functions and their derivatives to show how a two-point boundary value problem may be discretized. In the interval (a,b), suppose that the function u satisfies the ordinary differential equation

$$Lu=f(x), \tag{3.20}$$

with

$$Lu=-p(x)\frac{d^2u}{dx^2}+r(x)\frac{du}{dx}+q(x)u, \tag{3.21}$$

and the boundary conditions

$$\mu_1 u(a)+\nu_1 u'(a)=d_1, \qquad \mu_2 u(b)+\nu_2 u'(b)=d_2. \tag{3.22}$$

The requirement that the differential equation (3.20) be satisfied at the Gauss points within each interval leads to the system of linear equations

$$\mathbf{L}\mathbf{u}=\mathbf{f}, \tag{3.23}$$

where as before **u** is given by Eq. (3.14) and

$$\mathbf{f}=[d_1,f(\xi_{11}),f(\xi_{12}),f(\xi_{21}),\cdots,f(\xi_{N1}),f(\xi_{N2}),d_2]^T. \tag{3.24}$$

The matrix **L** is

$$\mathbf{L}=\begin{bmatrix} \boxed{\mathbf{L}_0} & & & \\ \boxed{\quad\mathbf{L}_1\quad} & & & \\ & \ddots & & \\ & & \boxed{\quad\mathbf{L}_N\quad} & \\ & & & \boxed{\mathbf{L}_{N+1}} \end{bmatrix}. \tag{3.25}$$

Here the 1×2 matrices $\mathbf{L}_0$ and $\mathbf{L}_{N+1}$ arise from the conditions (3.22) at the left and right endpoints, respectively, with

$$\mathbf{L}_0=[\mu_1,\nu_1/h_1], \qquad \mathbf{L}_{N+1}=[\mu_2,\nu_2/h_N]. \tag{3.26}$$

For $1 \leq i \leq N$, the 2×4 matrices $\mathbf{L}_i$ may be written

$$\mathbf{L}_i = \mathbf{D}_i(p)\mathbf{A}_i + \mathbf{D}_i(r)\mathbf{C}_i + \mathbf{D}_i(q)\mathbf{B}_i, \tag{3.27}$$

where

$$\mathbf{D}_i(g) = \begin{bmatrix} g(\xi_{i1}) & 0 \\ 0 & g(\xi_{i2}) \end{bmatrix}. \tag{3.28}$$

The linear set of equations (3.23) can be solved for the values of the function $u(x)$ at the Gauss points.

In the following sections, we shall use the spline collocation method to solve partial differential equations that arise in the theory of diatomic molecules. To give some insight into how the spline discretization procedure can be used to solve two-dimensional partial differential equations, we conclude this section by considering the problem of solving the following equation

$$-a(x,y)\frac{\partial^2 u}{\partial x^2} - a_d(x,y)\frac{\partial u}{\partial x} - b(x,y)\frac{\partial^2 u}{\partial y^2} - b_d(x,y)\frac{\partial u}{\partial y} + c(x,y)u = f(x,y). \tag{3.29}$$

We define a partitioning of the two coordinate axes x and y

$$a = x_0 < x_1 < x_2 \cdots < x_M = b, \tag{3.30}$$

$$c = y_0 < y_1 < y_2 \cdots < y_N = d. \tag{3.31}$$

Functions of x and y may be approximated using a basis which consists of products of the members of the Hermite basis considered previously. This approximation has the form

$$u(x,y) = \sum_{i=0}^{N}\sum_{j=0}^{N}[\alpha_{ij}v_i(x)v_j(y) + \beta_{ij}v_i(x)s_j(y) + \gamma_{ij}s_i(x)v_j(y) + \delta_{ij}s_i(x)s_j(y)]. \tag{3.32}$$

In the rectangular region $a \leq x \leq b$ and $c \leq y \leq d$, we shall denote the collocation points (ξ_i^x, ξ_j^y) with $i = 1,2,\cdots,2M$ and $j = 1,2,\cdots,2N$. The values of a function and its partial derivatives at the collocation points may be obtained using tensor products of the matrices $\mathbf{A}_x$, $\mathbf{B}_x$, and $\mathbf{C}_x$ with the matrices $\mathbf{A}_y$, $\mathbf{B}_y$ and $\mathbf{C}_y$. Here the subscripts x and y indicate that the corresponding matrices are the discrete representation of operations involving the x- and y-coordinates respectively. With this notation, the vector $\mathbf{u_G}$ consisting of the values of the function $u(x,y)$ at the collocation points can be written

$$\mathbf{u_G} = (\mathbf{B}_x \otimes \mathbf{B}_y)\mathbf{u}, \tag{3.33}$$

where

$$\begin{aligned} \mathbf{u} = [&\alpha_{00},\beta_{00},\alpha_{01},\beta_{01},\cdots,\alpha_{0N},\beta_{0N},\gamma_{00},\delta_{00},\cdots,\gamma_{0N},\delta_{0N}, \\ &\alpha_{10},\beta_{10},\cdots,\gamma_{1N},\delta_{1N},\cdots,\alpha_{M0},\beta_{M0},\cdots,\gamma_{MN},\delta_{MN}]^T, \end{aligned} \tag{3.34}$$

$$\mathbf{u_G} = [u(\xi_1^x,\xi_1^y), u(\xi_1^x,\xi_2^y),\cdots,u(\xi_M^x,\xi_N^y)]^T, \tag{3.35}$$

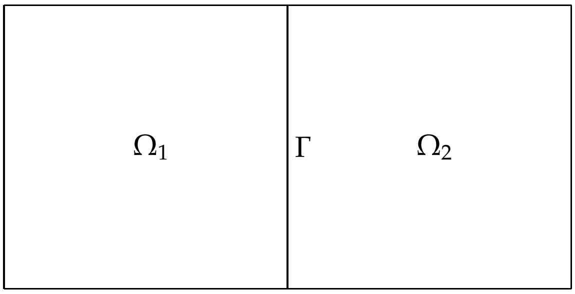

Figure 4: Region divided into 2 subregions by interface Γ.

and $\mathbf{B}_x \otimes \mathbf{B}_y$ is the tensor product of the matrices $\mathbf{B}_x$ and $\mathbf{B}_y$.

The requirement that Eq. (3.29) be satisfied at the Gauss points leads to the matrix equation

$$\begin{aligned}&\big[[\mathbf{D}_x(a(x,y))\mathbf{A}_x - \mathbf{D}_x(a_d(x,y))\mathbf{C}_x]\otimes\mathbf{B}_y + \mathbf{B}_x\otimes[\mathbf{D}_y(b(x,y))\mathbf{A}_y - \mathbf{D}_y(b_d(x,y))\mathbf{B}_y\big]\,\mathbf{u}\\ &+\mathbf{D}_{xy}(c(x,y))\mathbf{B}_x\otimes\mathbf{B}_y = \mathbf{f}_G.\end{aligned} \tag{3.36}$$

With the substitution, $\mathbf{v} = (\mathbf{B}_x \otimes \mathbf{B}_y)\mathbf{u}$, the above equation can be written

$$\hat{\mathbf{L}}\mathbf{v} = \mathbf{f}, \tag{3.37}$$

where $\hat{\mathbf{L}}$ is the matrix

$$\begin{aligned}\hat{\mathbf{L}} =& \big[[\mathbf{D}_x(a(x,y))\mathbf{A}_x - \mathbf{D}_x(a_d(x,y))\mathbf{C}_x]\otimes\mathbf{B}_y + \mathbf{B}_x\otimes[\mathbf{D}_y(b(x,y))\mathbf{A}_y - \mathbf{D}_y(b_d(x,y))\mathbf{C}_y]\\ &+\mathbf{D}_{xy}(c(x,y))\mathbf{B}_x\otimes\mathbf{B}_y\big](\mathbf{B}_x\otimes\mathbf{B}_y)^{-1}\\ =&\Big[\mathbf{D}_x(a(x,y))\mathbf{A}_x\mathbf{B}_x^{-1} - \mathbf{D}_x(a_d(x,y))\mathbf{C}_x\mathbf{B}_x^{-1}\Big]\otimes\mathbf{I}_y - \mathbf{I}_x\otimes\Big[\mathbf{D}_y(b(x,y))\mathbf{A}_y\mathbf{B}_y^{-1}\\ &+\mathbf{D}_y(b_d(x,y))\mathbf{C}_y\mathbf{B}_y^{-1}\Big] + \mathbf{D}_{xy}(c(x,y))\mathbf{I}_x\otimes\mathbf{I}_y.\end{aligned} \tag{3.38}$$

Here $\mathbf{I}_x$ and $\mathbf{I}_y$ are the identity matrices for the x- and y-partitions. If the operator on the left-hand side of Eq. (3.29) is self-adjoint, then the matrix $\hat{\mathbf{L}}$ is approximately symmetric [11].

4 Domain decomposition

Our effort here will be to give a brief outline of the domain decomposition theory for spline collocation [9]. This theory enables one to generate solutions of Schrödinger-like equations in the entire physical region from the solutions of boundary value problems in component subregions.

We begin by considering the simple problem of a region divided into two subregions by a vertical interface. A region of this kind is illustrated in Fig. 4. We denote a partial differential equation by

$$\mathbf{L}u(x,y)=f(x,y) \quad \text{for } a\leq x\leq b,\ c\leq y\leq d, \tag{4.1}$$

where **L** is a differential operator and $u(x,y)$ and $f(x,y)$ are functions of two variables. As shown in Fig. 4, we shall denote the two regions by Ω_1 and Ω_2 and the interface between the two regions by Γ. The solutions in these two regions will be denoted by $u_1(x,y)$ and $u_2(x,y)$, and the value of x at the interface between the two regions will be denoted by γ.

The domain decomposition method can be applied to the problem of solving partial differential equations with either Dirichlet or Neumann boundary conditions. Here, we shall suppose that the solution of Eq. (4.1) satisfies homogeneous Neumann conditions on the left and right boundaries and on the lower boundary while satisfying a homogeneous Dirichlet condition along the upper boundary

$$\begin{aligned} &\mathcal{D}_x u(a,y)=0 \quad y\in(c,d), && \mathcal{D}_x u(b,y)=0 \quad y\in(c,d),\\ &\mathcal{D}_y u(x,c)=0 \quad x\in[a,b], && u(x,d)=0 \qquad x\in[a,b], \end{aligned} \tag{4.2}$$

where $\mathcal{D}_x$ and $\mathcal{D}_y$ represent partial derivatives with respect to the x- and y- coordinates. We shall also suppose that the solution in the two regions satisfy the following continuity conditions at the interface between the two regions

$$u_1(\gamma,y)=u_2(\gamma,y), \qquad y\in(c,d), \tag{4.3}$$

$$\mathcal{D}_x u_1(\gamma,y)=\mathcal{D}_x u_2(\gamma,y), \quad y\in(c,d). \tag{4.4}$$

To use the domain decomposition method to solve Eq. (4.1) in the entire region with $a\leq x\leq b$ and $c\leq y\leq d$, we must find the value of the solution along the interface. Once u is known on the interface, the functions u_1 and u_2 in the two regions can be found independently. We shall denote the value of the solution along the interface by u_Γ and the Gauss points along the interface by $\mathcal{G}$. A number of important theorems have been proved that are relevant to spline collocation. One useful result is that a spline defined along the interface is uniquely determined by by its values at the Gauss points [10].

An equation for the solution on the interface can be obtained by resolving the function u into two functions $\hat{u}$ and $\tilde{u}$, which satisfy the same conditions as u along the exterior boundary

$$u(x,y)=\hat{u}(x,y)+\tilde{u}(x,y). \tag{4.5}$$

The properties of $\hat{u}$ and $\tilde{u}$ are complementary with $\hat{u}$ satisfying the same partial differential equation as u but being equal to zero on the interface between the two regions and $\tilde{u}$ satisfying the homogeneous form of the partial differential equation satisfied by u and is equal to u on the interface between the two regions. The function $\hat{u}_1$ satisfies the equation

$$\mathbf{L}\hat{u}_1(x,y)=f(x,y) \quad \text{for } a\leq x\leq\gamma,\ c\leq y\leq d, \tag{4.6}$$

with boundary conditions

$$\begin{aligned}
&\mathcal{D}_x\hat{u}_1(a,y)=0 \quad y\in(c,d), \qquad &&\mathcal{D}_y\hat{u}_1(x,c)=0 \quad x\in[a,\gamma],\\
&\hat{u}_1(x,d)=0 \qquad\; x\in[a,\gamma], \qquad &&\hat{u}_1(\gamma,y)=0 \qquad y\in(c,d),
\end{aligned} \tag{4.7}$$

while the function $\hat{u}_2$ satisfies the equation

$$\mathbf{L}\hat{u}_2(x,y)=f(x,y) \quad \text{for } \gamma\le x\le b,\; c\le y\le d, \tag{4.8}$$

with boundary conditions

$$\begin{aligned}
&\mathcal{D}_x\hat{u}_2(b,y)=0 \quad y\in(c,d), \qquad &&\mathcal{D}_y\hat{u}_2(x,c)=0 \quad x\in[\gamma,b],\\
&\hat{u}_2(x,d)=0 \qquad\; x\in[\gamma,b], \qquad &&\hat{u}_2(\gamma,y)=0 \qquad y\in(c,d).
\end{aligned} \tag{4.9}$$

Since the functions $\hat{u}_1$ and $\hat{u}_2$ satisfy boundary conditions that do not depend upon the nature of the solution along the interface, these functions can immediately be determined by solving the partial differential equations in the two regions.

The function $\tilde{u}_1$ satisfies the equation

$$\mathbf{L}\tilde{u}_1(x,y)=0 \quad \text{for } a\le x\le\gamma,\; c\le y\le d, \tag{4.10}$$

and the function $\tilde{u}_2$ satisfies the equation

$$\mathbf{L}\tilde{u}_2(x,y)=0 \quad \text{for } \gamma\le x\le b,\; c\le y\le d. \tag{4.11}$$

The conditions satisfied by $\tilde{u}_1$ and $\tilde{u}_2$ along the exterior boundaries are identical to the conditions satisfied $\hat{u}_1$ and $\hat{u}_2$. On the interface between the two regions $\tilde{u}_1$ and $\tilde{u}_2$ are equal to the solution of Eq. (4.1). We have

$$\tilde{u}_1(\gamma,y)=u_\Gamma \quad\text{and}\quad \tilde{u}_2(\gamma,y)=u_\Gamma, \quad \text{for } y\in(c,d). \tag{4.12}$$

The functions $\tilde{u}_1$ and $\tilde{u}_2$ can be determined once the solution along the interface is known.

We can obtain a condition upon the functions $\tilde{u}_1$ and $\tilde{u}_2$ at the interface by substituting Eq. (4.5) for the two regions into Eq. (4.4) and rearranging terms to obtain

$$\mathcal{D}_x\tilde{u}_1(\gamma,y)-\mathcal{D}_x\tilde{u}_2(\gamma,y)=\mathcal{D}_x\hat{u}_2(\gamma,y)-\mathcal{D}_x\hat{u}_1(\gamma,y). \tag{4.13}$$

To obtain the solution u along the interface, we define an interface operator K by the equation

$$Kv(y)=W_\Gamma \tag{4.14}$$

where the spline function $v(y)$ defined for $c\le y\le d$ satisfies the boundary conditions,

$$v'(c)=0 \quad\text{and}\quad v(d)=0.$$

The function W_Γ is defined by the equation

$$W_\Gamma(\xi)=\mathcal{D}_xV_1(\gamma,\xi)-\mathcal{D}_xV_2(\gamma,\xi), \quad \text{for } \xi\in\mathcal{G}. \tag{4.15}$$

Here ξ is a member of the set of Gauss points along the interface. The function V_1 satisfies the equation

$$\mathbf{L}V_1(x,y)=0 \quad \text{for } a\le x\le\gamma,\ c\le y\le d \tag{4.16}$$

with boundary conditions

$$\begin{aligned} &\mathcal{D}_x V_1(a,y)=0 \quad y\in(c,d), && \mathcal{D}_y V_1(x,c)=0 \quad x\in[a,\gamma],\\ &V_1(x,d)=0 \qquad x\in[a,\gamma], && V_1(\gamma,y)=v(y) \quad y\in(c,d), \end{aligned} \tag{4.17}$$

and the function V_2 satisfies the equation

$$\mathbf{L}V_2(x,y)=0 \quad \text{for } \gamma\le x\le b,\ c\le y\le d \tag{4.18}$$

with boundary conditions

$$\begin{aligned} &\mathcal{D}_x V_2(b,y)=0 \quad y\in(c,d), && \mathcal{D}_y V_2(x,c)=0 \quad x\in[\gamma,b],\\ &V_2(x,d)=0 \qquad x\in[\gamma,b], && V_2(\gamma,y)=v(y) \quad y\in(c,d). \end{aligned} \tag{4.19}$$

For a particular spline function $v(y)$ defined defined for $c\le y\le d$, the boundary conditions for the functions $V_1(x,y)$ and $V_2(x,y)$ are well defined and the function $W_\Gamma(\xi)$ is given by Eq. (4.15). If the function $v(y)$ is equal to the function u_Γ, which is the value of the solution of Eq. (4.1) along the interface, then the boundary conditions for the functions $V_1(x,y)$ and $V_2(x,y)$ are identical to the boundary conditions for the functions $\tilde{u}_1(x,y)$ and $\tilde{u}_2(x,y)$. The function $V_1(x,y)$ is then equal to $\tilde{u}_1(x,y)$ and the function $V_2(x,y)$ is equal to $\tilde{u}_2(x,y)$. Using Eqs. (4.15) and (4.13), one can then see that right-hand side of the interface equation (4.14) is equal to the right-hand side of Eq. (4.13). The interface equation may thus be written

$$Ku_\Gamma=\mathcal{D}_x\hat{u}_2(\gamma,y)-\mathcal{D}_x\hat{u}_1(\gamma,y), \tag{4.20}$$

and we may define Algorithm 4.1 for solving the partial differential equation (4.1) with boundary conditions (4.2).

Algorithm 4.1:

```
Step 1. Using $\hat{u}_1$ and $\hat{u}_2$ obtained by solving Eqs. (4.6) - (4.9), compute the right-hand side of Eq. (4.20).
Step 2. Solve Eq. (4.20) to find the solution of Eq. (4.1) along the interface.
Step 3. Solve Eqs. (4.10) and (4.11) to obtain the functions $\tilde{u}_1$ and $\tilde{u}_2$ and add these functions to $\hat{u}_1$ and $\hat{u}_2$ to obtain the solution $u$ in regions $\Omega_1$ and $\Omega_2$.
```

The interface equation (4.20) can most easily be solved using iterative methods. For the partial differential equations with variable coefficients that arise in the Hartree-Fock theory for diatomic molecules, the interface matrix is generally not symmetric. The interface equations can then be solved most efficiently using the pre-conditioned GMRES method.

5 A model problem

The domain decomposition methods we have described can be tested by using the states of a single-electron molecular ion. Self-adjoint equations for these states can be obtained by setting the direct and exchange terms equal to zero in Eqs. (2.14) and (2.20). For the hydrogen molecular ion H_2^+, the parameter Z which occurs in these equations has the value $Z_a+Z_b=2$, while the parameter Δ has the value $Z_a-Z_b=0$. A more useful model problem is provided by the singly ionized helium ion He^+ whose wave functions can be expressed analytically. For He^+, Z_a can be taken to be two and Z_b can be taken to be zero. Then,

$$Z=Z_a+Z_b=2, \quad \Delta=Z_a-Z_b=2.$$

Using spheroidal coordinates defined by Eq. (2.4) and the coordinate transformation (2.10), the wave function for the ground state of a He^+ ion centered at a can be written

$$u(\nu,\mu)=\left(\frac{Z^3}{\pi}\right)^{1/2}\exp\left[-\frac{1}{2}RZ_a(\cos\nu+\cosh\mu)\right]. \tag{5.1}$$

This wave function satisfies homogeneous Neumann boundary conditions on the vertical sides and on the lower boundary while satisfying a homogeneous Dirichlet boundary condition on the upper boundary. The orbital equation for the state (5.1) can be obtained by setting J_a, K_a, and m equal to zero in Eq. (2.14) to obtain

$$\begin{aligned}&-\sin\nu\sinh\mu\frac{\partial^2 u}{\partial\nu^2}-\cos\nu\sinh\mu\frac{\partial u}{\partial\nu}-\sin\nu\sinh\mu\frac{\partial^2 u}{\partial\mu^2}-\sin\nu\cosh\mu\frac{\partial u}{\partial\mu}\\&\quad+\sin\nu\sinh\mu(-RZ\xi+R\Delta\eta)u=\epsilon\sin\nu\sinh\mu\frac{R^2}{2}(\xi^2-\eta^2)u,\end{aligned} \tag{5.2}$$

where $Z=\Delta=2$ and $\epsilon=-Z^2/2$.

Coefficients in the above equation go zero on the left boundary when $\nu=0$, on the right boundary when $\nu=\pi$, and on the lower boundary when $\mu=0$. As a result, the differential operator on the left-hand of Eq. (5.2) is not positive definite; however, the operator will be positive definite in a subregion that does not include the exterior boundaries. Fig. 5 shows a partition of the entire region into nine parts. The operator on the left-hand side of Eq. (5.2) is both self-adjoint and positive definite in the the interior region which is denoted by Ω_{22} in the figure. The accuracy of the domain decomposition theory we have described can be tested by evaluating the right-hand side of Eq. (5.2) at the collocation points and comparing the solution of the equation with the analytical solution (5.1). The maximum errors obtained in each of the nine regions using a grid of 144 points in each direction are shown in Table 1.

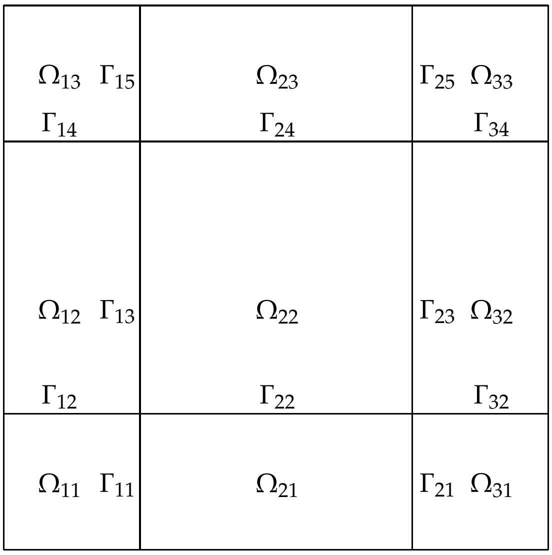

Figure 5: Region divided into nine subregions by interior boundaries. The subregions are denoted by Ω_{ij} and the interfaces denoted by Γ_{ij}.

Table 1: The maximum error for each of the nine regions shown together with the convergence rate. A convergence rate of four would mean that the maximum error decreased by a factor of $2^4=16$ if the step-size decreased by a factor of two.

Grid pts $n\times n$	u	u_x	u_y	u_{xy}
Ω_{11}	3.3×10^{-7}	1.9×10^{-7}	2.6×10^{-7}	9.7×10^{-8}
Convergence rate	4.42	4.17	4.50	7.36
Ω_{21}	6.5×10^{-7}	4.6×10^{-7}	5.1×10^{-7}	3.7×10^{-7}
Convergence rate	3.86	4.58	3.91	5.57
Ω_{31}	1.5×10^{-6}	4.5×10^{-7}	1.2×10^{-6}	3.9×10^{-7}
Convergence rate	3.44	4.60	3.71	3.50
Ω_{12}	1.9×10^{-7}	9.3×10^{-8}	3.2×10^{-7}	1.0×10^{-7}
Convergence rate	4.51	4.15	4.45	7.26
Ω_{22}	2.2×10^{-7}	4.5×10^{-7}	4.1×10^{-7}	7.9×10^{-7}
Convergence rate	4.48	4.51	4.18	6.21
Ω_{32}	2.5×10^{-7}	4.4×10^{-7}	1.0×10^{-6}	7.8×10^{-7}
Convergence rate	4.54	4.56	3.65	4.47
Ω_{13}	5.3×10^{-8}	1.8×10^{-8}	2.6×10^{-7}	7.6×10^{-8}
Convergence rate	4.25	2.93	4.28	2.78
Ω_{23}	4.6×10^{-8}	8.3×10^{-8}	2.3×10^{-7}	4.4×10^{-7}
Convergence rate	4.41	4.61	4.43	4.61
Ω_{33}	7.3×10^{-8}	8.3×10^{-8}	3.8×10^{-7}	4.4×10^{-7}
Convergence rate	4.47	4.64	4.50	4.62

6 The eigenvalue problem

To implement the Hartree-Fock theory for diatomic molecules, one must solve partial differential equations and eigenvalue problems. The Hartree-Fock equations themselves are eigenvalue equations that can be solved with Lanczos or Arnoldi methods in which an operator acts successively upon a function representing a single-electron state. A modern description of iterative methods for solving eigenvalue problems can be found in the books by Trefethen and Bau [11] and by Bai et al. [12].

Standard eigenvalue problems are of the general form

$$Lu=\epsilon u, \tag{6.1}$$

where L is a differential operator, u is a function of the spatial coordinates, and ϵ is an eigenvalue. The operator L is typically represented by a large sparse matrix, $\mathbf{L}$, and the wave functions are represented by column vectors, $\mathbf{u}$. The Lanczos and the Arnoldi methods can be used effectively to find eigenvalues in the outer part of the spectrum. They can, in particular, find a well-separated maximum eigenvalue and the eigenvector associated with that eigenvalue. To find the eigenvectors associated with lower-lying eigenvalues, one can first subtract a term $\mathbf{I}\sigma\mathbf{u}$ from each side of the eigenvalue equation to obtain

$$(\mathbf{L}-\sigma\mathbf{I})\mathbf{u}=(\epsilon-\sigma)\mathbf{u}, \tag{6.2}$$

where $\mathbf{I}$ is the identity matrix and the constant σ is typically chosen to be slightly less that the eigenvalue of interest. If σ is not an eigenvalue, one can invert the above equation to obtain

$$(\mathbf{L}-\sigma\mathbf{I})^{-1}\mathbf{u}=(\epsilon-\sigma)^{-1}\mathbf{u}. \tag{6.3}$$

The equation for the eigenvalue ϵ of $\mathbf{L}$ is thus converted into the eigenvalue problem for a well-separated maximum eigenvalue of $(\mathbf{L}-\sigma\mathbf{I})^{-1}$.

The matrix vector products,

$$(\mathbf{L}-\sigma\mathbf{I})^{-1}\mathbf{x}=\mathbf{z}, \tag{6.4}$$

which occur in the algorithm for obtaining the eigenvalue are evaluated by solving the linear system

$$(\mathbf{L}-\sigma\mathbf{I})\mathbf{z}=\mathbf{x}, \tag{6.5}$$

and not by computing the inverse of the matrix. Using inverted forms of the Lanczos or Arnoldi methods thus has the consequence that one must solve a set of linear equations to evaluate the product of the inverted matrix times a vector. The domain decomposition theory described in previous sections provides an efficient means of evaluating the matrix-vector products that occur in Lanczos and Arnoldi algorithms for the eigenvalues and eigenvectors of the Hartree-Fock theory.

The basic strategy we shall use for obtaining the eigenvalues of a matrix is to build an orthogonal basis of vectors by solving a sequence of linear systems of the above form. In this basis the large eigenvalue problem will be represented by a small eigenvalue problem. Some of the eigenvalues of this small problem will be good approximations to some of the eigenvalues of the large problem.

Algorithm 6.1 is a formulation of the Arnoldi iteration applied to an unsymmetric matrix $\mathbf{A}$, which in our work corresponds to the matrix $(\mathbf{L}-\sigma\mathbf{I})^{-1}$ of the inverted eigenvalue problem.

Algorithm 6.1: Arnoldi Algorithm

```
$\mathbf{b}$ = arbitrary, $\mathbf{q}_1=\mathbf{b}/\|\mathbf{b}\|$
for $n=1,2,3,\cdots$ do
    $\mathbf{v}=\mathbf{A}\mathbf{q}_n$                 $\mathbf{A}$ enters here
    for $j=1,\cdots,n$ do
        $h_{jn}=\mathbf{q}_j^T\mathbf{v}$            $T$ denotes transpose
        $\mathbf{v}=\mathbf{v}-h_{jn}\mathbf{q}_j$
    end
    $h_{n+1,n}=\|\mathbf{v}\|$
    $\mathbf{q}_{n+1}=\mathbf{v}/h_{n+1,n}$
end
```

Algorithm 6.1, which is a modified Gram-Schmidt procedure, generates an orthonormal basis of vectors, $\mathbf{q}_1$, $\mathbf{q}_2$, $\cdots$. In this basis $\mathbf{A}$ is represented by an upper Hessenberg matrix constructed from the h_{jk}-elements.

For a particular value of n, the matrix $\mathbf{Q}_n$ may be defined as the $m\times n$ matrix whose columns are the first n basis vectors, and $\mathbf{Q}_{n+1}$ may be defined as the $m\times(n+1)$ matrix whose columns are the first $n+1$ basis vectors. We have

$$\mathbf{Q}_n=[\mathbf{q}_1,\cdots,\mathbf{q}_n] \quad\text{and}\quad \mathbf{Q}_{n+1}=[\mathbf{q}_1,\cdots,\mathbf{q}_n,\mathbf{q}_{n+1}]. \tag{6.6}$$

Similarly, we may use the coefficients h_{jn} generated by the Arnoldi iterations to define matrices $\mathbf{H}_n$ and $\tilde{\mathbf{H}}_n$

$$\mathbf{H}_n=\begin{bmatrix} h_{11} & h_{12} & \cdots & h_{1n} \\ h_{21} & h_{22} & & h_{2n} \\ & \ddots & \ddots & \vdots \\ & & h_{n,n-1} & h_{nn} \end{bmatrix},\quad \tilde{\mathbf{H}}_n=\begin{bmatrix} h_{11} & h_{12} & \cdots & h_{1n} \\ h_{21} & h_{22} & & h_{2n} \\ & \ddots & \ddots & \vdots \\ & & h_{n,n-1} & h_{nn} \\ & & & h_{n+1,n} \end{bmatrix}. \tag{6.7}$$

The only difference between the matrices, $\mathbf{H}_n$ and $\tilde{\mathbf{H}}_n$, is the last row of $\tilde{\mathbf{H}}_n$. Denoting by ${\mathbf{e}_n}^T$ the unit row vector $[0,\cdots,0,1]$ with a one in the n-th place, the relation between the two matrices may then be written

$$\tilde{\mathbf{H}}_n=\begin{bmatrix} \mathbf{H}_n \\ \mathbf{e}_n^T h_{n+1,n} \end{bmatrix}. \tag{6.8}$$

The matrices $\mathbf{Q}_n$, $\mathbf{Q}_{n+1}$, and $\tilde{\mathbf{H}}_n$ may be shown to satisfy the equation

$$\mathbf{A}\mathbf{Q}_n = \mathbf{Q}_{n+1}\tilde{\mathbf{H}}_n. \tag{6.9}$$

Using Eqs. (6.6) and (6.8), this last equation can be written

$$\begin{aligned}\mathbf{A}\mathbf{Q}_n &= [\mathbf{Q}_n, \mathbf{q}_{n+1}] \begin{bmatrix} \mathbf{H}_n \\ \mathbf{e}_n^T h_{n+1,n} \end{bmatrix} \\ &= \mathbf{Q}_n\mathbf{H}_n + \mathbf{q}_{n+1}\mathbf{e}_n^T h_{n+1,n}. \end{aligned} \tag{6.10}$$

Suppose now that $\mathbf{s}$ is a normalized eigenvector, with corresponding eigenvalue ν, of $\mathbf{H}_n$

$$\mathbf{H}_n\mathbf{s} = \nu\mathbf{s}. \tag{6.11}$$

Multiplying Eq. (6.10) from the right-hand side by the eigenvector $\mathbf{s}$ and taking the first term on the right-hand side of the resulting equation over to the left-hand side, we obtain

$$\mathbf{A}\mathbf{Q}_n\mathbf{s} - \nu\mathbf{Q}_n\mathbf{s} = \mathbf{q}_{n+1} s_n h_{n+1,n}. \tag{6.12}$$

The norm of the vectors on the left-and right-hand sides of the above equation may now be set equal to each other. Using the fact that the basis vector q_{n+1} is normalized, we get

$$||\mathbf{A}\mathbf{Q}_n\mathbf{s} - \nu\mathbf{Q}_n\mathbf{s}|| = |s_n| h_{n+1,n}. \tag{6.13}$$

The residual error of the transformed eigenvector $\mathbf{Q}_n\mathbf{s}$ is thus equal to $|s_n|h_{n+1,n}$, where $h_{n+1,n}$ is the last coefficient produced by the Arnoldi iteration scheme and $|s_n|$ is the absolute value of the last component of the eigenvector $\mathbf{s}$. Good approximations are usually characterized by small $|s_n|$. The reason is that the approximate eigenvector, $\mathbf{Q}_n\mathbf{s}$, is a linear combination of the vectors in $\mathbf{Q}_n$. If the first $n-1$ vectors in $\mathbf{Q}_n$ produce a good approximation only the tiny adjustment, $\mathbf{q}_n s_n$ is needed to make the approximation even better.

The integer m giving the number of rows of the collocation matrix $\mathbf{A}$ is typically equal to about twenty thousand for the Hartree-Fock theory of diatomic molecules, while the integer n corresponding to the number of Arnoldi iterations is typically equal to five. For all of the cases we have considered, the Arnoldi iteration scheme converges very rapidly giving a small matrix whose eigenvalues and eigenvectors can be easily obtained using standard LAPACK routines.

The effectiveness of the Lanczos and Arnoldi schemes for finding the eigenvalues and eigenvectors of the Hartree-Fock equations can be studied by considering the simple model problem described in the previous section. Using the spline collocation method to discretize the orbital equation (5.2) for the He^+ ion, we obtain

$$\mathbf{L}\mathbf{u} = (\epsilon - \sigma)\mathbf{D}\left(\frac{R^2}{2}(\xi^2 - \eta^2)\right)(\mathbf{B}_\nu \otimes \mathbf{B}_\mu)\mathbf{u}, \tag{6.14}$$

where the matrix $\mathbf{L}$ is

$$\begin{aligned}\mathbf{L}=&\big[\mathbf{D}(\sin\nu\sinh\mu)\mathbf{A}_\nu-\mathbf{D}(\cos\nu\sinh\mu)\mathbf{C}_\nu\big]\otimes\mathbf{B}_\mu+\mathbf{B}_\nu\otimes[\mathbf{D}(\sin\nu\sinh\mu)\mathbf{A}_\mu\\&-\mathbf{D}(\sin\nu\cosh\mu))\mathbf{B}_\mu\big]+\mathbf{D}(\sin\nu\sinh\mu(-RZ\xi+R\Delta\eta)\mathbf{B}_\nu\otimes\mathbf{B}_\mu.\end{aligned}\tag{6.15}$$

The matrices of the form $\mathbf{D}(f\nu,\mu)$ in these last equations are diagonal matrices with the values of the corresponding function $f(\nu,\mu)$ at the Gauss points along the diagonal.

Eq. (6.14) defines a generalized eigenvalue problem. The equation can be converted into a simple eigenvalue problems by making the substitution

$$\mathbf{v}=(\mathbf{B}_\nu\otimes\mathbf{B}_\mu)\mathbf{u}.\tag{6.16}$$

This leads to the equation

$$\hat{\mathbf{L}}\mathbf{v}=(\epsilon-\sigma)\mathbf{D}\left(\frac{R^2}{2}(\xi^2-\eta^2)\right)\mathbf{v},\tag{6.17}$$

where

$$\hat{\mathbf{L}}=\mathbf{L}(\mathbf{B}_\nu\otimes\mathbf{B}_\mu)^{-1}.\tag{6.18}$$

The substitution $\mathbf{w}=\mathbf{D}(R^2(\xi^2-\eta^2)/2)^{1/2}\mathbf{v}$ then gives

$$\left[\mathbf{D}\left(\frac{R^2}{2}(\xi^2-\eta^2)\right)^{-1/2}\hat{\mathbf{L}}\mathbf{D}\left(\frac{R^2}{2}(\xi^2-\eta^2)\right)^{-1/2}\right]\mathbf{w}=(\epsilon-\sigma)\mathbf{w}.\tag{6.19}$$

We can then invert this last equation to obtain

$$\left[\mathbf{D}\left(\frac{R^2}{2}(\xi^2-\eta^2)\right)^{1/2}\hat{\mathbf{L}}^{-1}\mathbf{D}\left(\frac{R^2}{2}(\xi^2-\eta^2)\right)^{1/2}\right]\mathbf{w}=\left(\frac{1}{\epsilon-\sigma}\right)\mathbf{w}.\tag{6.20}$$

While the matrices, $\mathbf{A}$, $\mathbf{B}$, and $\mathbf{C}$, described in Section 3 of this article are not symmetric, the matrix $\hat{\mathbf{L}}=\mathbf{L}(\mathbf{B}_\nu\otimes\mathbf{B}_\mu)^{-1}$ is approximately symmetric. This result has been shown previously [13] and confirmed by explicitly constructing a representative number of rows and columns of the matrix. The matrix $\hat{\mathbf{L}}^{-1}$ is also approximately symmetric. If the energy shift σ is sufficiently close to the eigenvalue ϵ, $1/(\epsilon-\sigma)$ will be a well-separated maximum eigenvalue, which can be obtained by applying the Lanczos or Arnoldi algorithms to the matrix within brackets on the left-side of Eq. (6.20).

The Lanczos iteration scheme is the Arnoldi specialized to the case where the matrix is symmetric. The reduced $\mathbf{H}_n$ matrix, which is then both symmetric and Hessenberg, is tridiagonal. This means that in the inner loop of the Arnoldi iteration, the limits 1 to n can be replaced with the limits $n-1$ to n. We shall use the customary notation for the Lanczos method in which the diagonal elements of the reduced matrix $\mathbf{H}_n$ are denoted by α_n and the elements below and above the diagonal of the reduced matrix are denoted by β_n. The $\mathbf{H}_n$ matrix then is

$$\mathbf{H}_n = \begin{bmatrix} \alpha_1 & \beta_1 & & & \\ \beta_1 & \alpha_2 & \beta_2 & & \\ & \beta_2 & \alpha_3 & \ddots & \\ & & \ddots & \ddots & \beta_{n-1} \\ & & & \beta_{n-1} & \alpha_n \end{bmatrix}, \tag{6.21}$$

and the **Lanczos Algorithm** becomes Algorithm 6.2.

Algorithm 6.2: Lanczos Algorithm

```
$\beta_0 = 0$, $\mathbf{q}_0 = \mathbf{0}$, $\mathbf{b}$ = arbitrary, $\mathbf{q}_1 = \mathbf{b}/\|\mathbf{b}\|$
for $n = 1,2,3,\cdots$ do
    $\mathbf{v} = \mathbf{A}\mathbf{q}_n$                $\mathbf{A}$ enters here
    $\alpha_n = \mathbf{q}_n^T \mathbf{v}$
    $\mathbf{v} = \mathbf{v} - \beta_{n-1}\mathbf{q}_{n-1} - \alpha_n \mathbf{q}_n$
    $\beta_n = ||\mathbf{v}||$
    $\mathbf{q}_{n+1} = \mathbf{v}/\beta_n$
end
```

For each step, the most computationally demanding operation is the matrix-vector multiplication, which for the inverse Lanczos and Arnoldi algorithms requires the solution of a large set of linear equations. Each iteration also includes a scalar product and a few vector operations. While the Arnoldi iterations scheme explicitly orthogonalizes each new **q**-vector with the previous vectors, the Lanczos scheme depends upon the matrix being symmetric in which case it suffices to orthogonalize with the previous two vectors. Any lack of asymmetry of the matrix can be expected to lead to a lack of orthogonality of the Lanczos basis vectors.

The inverse Lanczos method may be used to obtain an approximation of the eigenvalues and eigenvectors of the matrix $(\mathbf{L}-\sigma\mathbf{I})^{-1}$ and hence to an approximation of the eigenvectors and eigenvalues of the matrix **L**. For both the Arnoldi and Lanczos iteration schemes, the accuracy of the eigenvectors can be estimated using Eq. (6.13).

The accuracy of the Lanczos algorithm has been studied by a number of authors. Ericsson and Ruhe have shown [14] that if ν is an eigenvalue of $(\mathbf{L}-\sigma\mathbf{I})^{-1}$ and ϵ is the corresponding exact eigenvalue of **L**

$$|\epsilon - (\sigma + \nu^{-1})| \leq \beta_n |s_n| / \nu^2. \tag{6.22}$$

The Lanczos algorithm can thus be used to produces an accurate approximation of the eigenvalues of **L**. To obtain eigenvectors of the matrix **L** at a comparable level of accuracy, though, one must add a little of the next Lanczos iteration to the eigenvector

$$\mathbf{Q}_n \mathbf{s} + (\beta_n s_n / \nu)\, \mathbf{q}_{n+1}. \tag{6.23}$$

We have tested the accuracy of the Lanczos algorithm for obtaining the lowest eigenvalue of the helium He^+ ion using a grid of 64 points in each direction. The results are shown in Table 2. The exact nonrelativistic value of the energy is 2.0 atomic units. For each iteration n, the energy eigenvalue is shown in the second column of the table, while the error is shown in the third column. The error was estimated for each iteration by using Eq. (6.22) and the final eigenvector was obtained using Eq. (6.23). The maximum difference between the calculated and analytic eigenvector for all of the nine regions was one part in 10^{-5}.

Table 2: The eigenvalue for each iteration of the Lanczos algorithm shown together with an estimate of the error obtained using Eq. (6.22).

n	ϵ	error
1	-1.76101	0.477
2	-1.99988	3.000×10^{-3}
3	-1.99998	5.327×10^{-5}
4	-1.99998	1.714×10^{-5}
5	-1.99998	4.187×10^{-4}
6	-2.00005	6.682×10^{-5}
7	-2.00005	9.635×10^{-6}

When the Lanczos algorithm is applied to a symmetric matrix, round off errors cause the $\mathbf{q}$-vectors to loose orthogonality as one approaches convergence. This will cause copies of already converged eigenvalues to appear. There are several ways to cope with this loss of orthogonality [12]. Our applications of the Lanczos method indicate, though, that the small unsymmetric part of the operator $\hat{\mathbf{L}}$ causes departure from orthogonality for a small number of iterations before one has approached convergence. For this reason, we do not recommend the Lanczos method to find the eigenvalues and eigenvectors for the problems discussed in this article.

The Arnoldi algorithm, which does not depend upon the matrix $\hat{\mathbf{L}}$ being symmetric, produces more convincing results. The lowest eigenvalue of the helium He^+ ion was obtained using the Arnoldi algorithm with a grid of 64 points in each direction producing the results shown in Table 3.

Table 3: The eigenvalue for each iteration of the Arnoldi algorithm shown together with an estimate of the error obtained using Eq. (6.22).

n	ϵ	error
1	-1.76101	0.477
2	-1.99987	2.998×10^{-3}
3	-1.99996	5.069×10^{-5}
4	-1.99996	8.622×10^{-7}

As for the Lanczos iterations, the energy eigenvalue is shown in the second column of the table, while the error is shown in the third column. Unlike the numerical basis generated by the Lanczos iterations discussed earlier, the numerical basis produced by the Arnoldi scheme has a high level of orthogonality. The eigenvalues of the Hessenberg matrix produces by the Arnoldi iteration scheme were all distinct as they should be. At the conclusion of the Arnoldi iterations, Eq. (6.23) was still used to calculate the final eigenvector. This is reasonable since the matrix $\hat{\mathbf{L}}$ is approximately symmetric and it can be shown that the mathematics is still valid. The maximum difference between the calculated and analytic eigenfunction for all of the nine regions was one part in 10^{-5}.

7 Discussion

We would now like to discuss briefly our results in the context of other numerical Hartree-Fock calculations for diatomic molecules. The methods one uses to perform numerical calculations on diatomic molecules depends upon how one discretizes the Hartree-Fock equations. The Hartree-Fock equations can be discretized by using finite difference approximations of the derivatives or by using the spline collocation or Galerkin methods. The first numerical calculations for diatomic molecules, which were carried out by E. A. McCullough Jr [3], used a partial wave expansion of the single-electron wave functions,

$$\psi(\xi,\eta,\phi)=\frac{e^{im\phi}}{(2\pi)^{1/2}}\sum_{\ell}X_{\ell}(\xi)P_{\ell}(\eta), \tag{7.1}$$

where the variables ξ and η are the same as the spheroidal coordinates we have used in our calculations. Expanding the wave functions in partial waves led to a coupled set of ordinary differential equation, which were solved using finite difference approximations of the derivatives. McCullough considered a number of model problems to study the convergence properties of the expansion over ℓ in Eq. (7.1). He found that 20 to 25 terms were generally sufficient to obtain the desired level of accuracy. McCulllough developed an efficient multiconfiguration Hartree-Fock (MCHF) program patterned after the atomic MCHF program of C. F. Fischer [1].

Another approach for diatomic molecules that does not rely upon a partial wave expansion of the wave functions was later developed by Laaksonen, Pyykko and Sundholm [4] and by J. Kobus et al [5]. In this approach, the wave functions were assumed to be of the general form

$$\psi(\xi,\eta,\phi)=\frac{e^{im\phi}}{(2\pi)^{1/2}}u(\xi,\eta) \tag{7.2}$$

and the Hartree-Fock equations were reduced to partial differential equations for the function $u(\xi,\eta)$. Using a 9-point central difference approximation for the first and second derivatives, Laaksonen and his collaborators were able to obtain more accurate results than the results found previously by McCullough; however, the linear algebra methods employed by Laaksonen et al were not optimal. Using a form of the Hartree-Fock equations, which are not self-adjoint, they obtained a discrete form of the differential equations with non-symmetric matrices. The associate linear equations were solved with the successive over-relaxation (SOR) method using typically several hundreds of iterations.

In two previous articles [6,7], we have shown that the Hartree-Fock equation for a diatomic article can be discretized using the orthogonal spline collocation method. Recently, Bialecki and Dryja have developed a theory of domain decomposition for orthogonal spline collocation [9] that enables us to use fast Krylov methods in the broad interior of the variable domain while using Gaussian elimination near the boundaries. The numerical strategy discussed in the present article depends upon this domain decomposition theory. The convergence rate of the model calculations reported in this paper are of fourth order since we have used fourth-order splines. We intend in the future to perform calculations with higher-order splines to achieve a higher level of accuracy.

A promising new method for solving the Hartree-Fock equations for diatomic molecules has more recently been developed by Artemyev et al [15]. Using the equations,

$$\begin{aligned} \eta &= \cos u \qquad \text{for } 0 \le \nu \le \pi, \\ \xi &= \cosh v \qquad \text{for } 0 \le \mu \le \infty, \end{aligned}$$

to express the spheroidal coordinates ξ and η in terms of new independent variables u and v, they have develop a spline Galerkin formalism with basis functions

$$\tau^m_{n,\ell} = B_{n,k}(u) P_{\ell,m}(\cos v),$$

where $B_{n,k}$ is the nth B-spline of order k and $P_{\ell,m}(\cos v)$ is an associated Legendre polynomial. Artemyev and his collaborators thus use B-splines for one variable and Legendre polynomials as McCullough did for the other variable. Artemyev et al have not given enough details for us to be able to evaluate the linear algebra component of their theory.

One would hope that Artemyev and his collaborators will eventually use a more standard finite element approach with basis functions having local support in both coordinates directions. Such a spline basis of order order k should yield a convergent rate of h^k. Also, the discretized form of the Hartree-Fock equation should then be symmetric. Using Legendre polynomials has the effect of making the matrices dense and likely reduces the numerical accuracy of the calculation. Slowly converging partial wave expansions have caused many difficulties in atomic and molecular physics.

An important advantage of the theory described by Artemyev and his collaborators is that they are able to include higher-order correlation effects using the basis generated in the Hartree-Fock calculation. The inclusion of correlation effects is essential for obtaining a realistic description of atoms and molecules.

Some idea of the success the mullticonfiguration Hartree-Fock theory is likely to have for molecules can be obtained by considering the more established area of atomic physics. For atoms, the multi-configuration Hartree-Fock theory generally does very well in including the most strongly interacting configurations but has difficulty including more weakly interacting configurations. Conversely, many-body perturbation theory easily includes weakly coupled configurations but has difficulties including strongly interacting configurations. Some years ago one of the present authors (J.C.M.) and C. F. Fischer collaborated in calculations in which they combined the multiconfiguration Hartree-Fock theory and many-body perturbation theory [16]. A multiconfiguration Hartree-Fock calculation was carried out using the most strongly interacting configurations and a set of pair equations was then solved to include the cumulative effect of more weakly interacting configurations. This is the strategy we intend to employ ourselves for including including correlation effects. We intend to develop an efficient multiconfiguration Hartree-Fock program which can be used to include a number of strongly interacting configuration, and we then intend to solve pair equations to include the more weakly interacting configurations. While the pair equation for atoms can be reduced to a two-variable partial differential equation, the pair equation for diatomic molecules involves five independent variables. Rather than try to solve partial differential equations with five variables, we plan to use the method developed by S. Salomonson and P. Oster who have generated solutions of the pair equation from a numerical basis [17]. This approach is qualitatively similar to the work of Artemyev et al because it would include the effects of correlation using a single-electron basis.

8 Conclusion

We have found that by using the spline collocation method together with the newly developed theory of domain decomposition we can obtain very accurate solutions of the partial differential equations and eigenvalue equations that arise in the Hatree-Fock theory for diatomic molecules. In a future paper, we will discuss the solution of Poison-like equations to evaluate the direct- and exchange terms in the Hartree-Fock equations and apply this theory to atoms and molecules having several electrons.

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