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Grid Based Solutions of the N-Particle Schroedinger Equation

Christopher R. Anderson

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Department of Mathematics
University of California, Los Angeles
Los Angeles, CA. 90095-1555

Abstract

In this paper we present discretization techniques that can be combined to create completely grid based computational methods for the evaluation of approximate solutions of the the N-particle Schroedinger equation. As an example of the use of these discretization techniques, we describe an implementation of a Full Configuration Interaction (FCI) procedure for computing the solution of the N-particle Schroedinger equation for systems with a small number of electrons. As a demonstration of the utility of using grid based computational procedures, we give an example of the computation of the dissociation of H_2 using a computed, configuration dependent, orbital basis set.

1 Introduction

In this paper we describe a collection of discretization techniques that can be used to develop completely grid based computational methods to create approximate solutions of the N-particle Schroedinger equation. The techniques we describe were primarily developed to create implementations of approximation methods that are wave-function based; methods ranging from Hartree-Fock and its extensions to the Full Configuration Interaction (FCI) procedure. However, due to the similarity of many of the computational tasks, these computational techniques may be of use for other types of methods such as those associated with density functional theory.

In wave function based methods the N-particle wave function is typically approximated by a single product or sum of products of spin orbital basis functions (see [19] for a good introduction to these methods). The spin orbital basis functions are functions of four variables and are themselves product functions consisting of an orbital basis function of three spatial coordinates and a spin function of a single spin coordinate. Accurate computations using a particular set of spin orbital basis functions depends critically on the choice of spatial orbital basis functions. In addition, accurate methods for the evaluation of integral and differential functionals of the basis functions are required to set up the discrete system of linear or non-linear equations that determine which product, or which coefficients in a sum of products, gives an accurate approximation to the N-particle wave function. For many problems good orbital basis functions can be found that have analytic representations, a feature that greatly facilitates evaluating the required functionals. However, there are also situations when good analytical orbital basis functions are not known, or when analytic representations are inconvenient to work with — such as when one desires to determine wave functions in the presence of an external potential that is only known by values on a computational grid. In these latter situations, the use of grid based orbitals provides an alternate representation that can facilitate the development of methods that adaptively determine good orbital basis functions and/or methods that can easily accommodate a wider range of external potentials. Additionally, since grid based orbitals can be easily transformed to an orthonormal set, many of the required computations involving the orbitals can be simplified.

While the idea of using grid based orbitals is simple to state, there are significant problems that one encounters when one seeks to develop methods that utilize them [11]. In particular, it is necessary to develop computational techniques for creating grid based approximations of orbital functionals that have high order rates of convergence, techniques that are capable of accommodating singular potentials, and techniques that make use of a finite computational domain to evaluate solutions of problems in infinite domains. In this paper we describe computational techniques for grid based orbitals that satisfy these requirements. These techniques are described in the context of a presentation of a completely grid based implementation of the FCI procedure for computing the wave functions of the Born-Oppenheimer approximation of the N-particle Schroedinger equation.

For a demonstration of the utility of a completely grid based approach we use the example of computing electronic structure as H_2 is dissociated. In this example, we highlight one of the advantageous features of the grid based approach, namely the capability to create and utilize an orbital basis that is configuration dependent. Specifically, we utilize a particular type of orbital basis set, smoothed “bare atomic molecular orbitals” (BAMOs), that are a natural generalization to polyatomic configurations of the widely used hydrogenic orbitals for single atoms.

In the first section we give a brief overview of the FCI procedure and identify the mathematical tasks that are required for the construction of the equations that determine the coefficients of an expansion of the N-particle wave function in a Slater determinant basis. In the second section we describe the computational techniques that are used carry out these computational tasks, and in the third section we present the example that demonstrates the construction and use of the smoothed bare atomic molecular orbitals to evaluate the electronic configuration of H_2 as it is dissociated.

2 The Full Configuration Interaction (FCI) Procedure

The computational procedures presented in this paper are described in the context of a completely grid based computational method for determining the eigenfunctions and eigenvalues of the operator associated with the Born-Oppenheimer approximation to time-independent N-particle Schroedinger equation. In atomic units, this problem takes the form

$$\mathrm{H}\Psi = \lambda\Psi \tag{1}$$

where H is the linear operator

$$\mathrm{H} \;=\; -\frac{1}{2}\sum_{i=1}^{\mathrm{N}}\Delta_i - \sum_{i=1}^{\mathrm{N}}\sum_{\mathrm{A}=1}^{\mathrm{P}}\frac{Z_{\mathrm{A}}}{|r_i - r_{\mathrm{A}}|} + \sum_{i=1}^{\mathrm{N}}\sum_{j>i}^{\mathrm{N}}\frac{1}{|r_i - r_j|} \tag{2}$$

where the P nuclei have charges Z_{A} and are located at r_{A}. $\Psi = \Psi(\tilde{r}_1, \, \tilde{r}_2, \, \ldots \, \tilde{r}_N)$ is the N-particle eigenfunction where $\tilde{r}_i = (r_i, \omega_i)$ with $r_i \in \mathrm{R}^3$ being the spatial coordinate and ω_i being the spin coordinate of the ith particle. In addition to being an eigenfunction of H, Ψ must also be anti-symmetric with respect to the interchange of any pair of electron coordinates;

$$\Psi(\tilde{r}_1, \ldots, \tilde{r}_p, \ldots, \tilde{r}_q \ldots \tilde{r}_{\mathrm{N}}) \;=\; -\Psi(\tilde{r}_1, \ldots, \tilde{r}_q, \ldots, \tilde{r}_p \ldots \tilde{r}_{\mathrm{N}}) \qquad \text{for all } p, q \in 1..N$$

The general methodology that underlies the computational procedure described here is a full configuration interaction (FCI) procedure using orthonormal spatial orbitals [19]. Assuming a set of M orthonormal functions of R^3, "an orbital basis set", $\{\phi_j\}_{j=1}^{\mathrm{M}}$, and two orthonormal functions of the spin coordinate, $\alpha(\omega)$ and $\beta(\omega)$ one constructs the 2M "spin orbitals",

$$\begin{aligned} \chi_{2j-1}(\tilde{r}) &= \phi_j(\vec{r})\alpha(\omega) \\ \chi_{2j}(\tilde{r}) &= \phi_j(\vec{r})\beta(\omega) \end{aligned} \tag{3}$$

for $j = 1, \ldots \mathrm{M}$. Associated with a distinct set of N spin orbitals, one can construct a Slater determinant basis function,

$$\vec{v}(\tilde{r}_1,\, \tilde{r}_2,\, \ldots\, \tilde{r}_N) \;=\; \det \begin{pmatrix} \chi_1(\tilde{r}_1) & \chi_2(\tilde{r}_1) & \cdots & \chi_N(\tilde{r}_1) \\ \chi_1(\tilde{r}_2) & \chi_2(\tilde{r}_2) & \cdots & \chi_N(\tilde{r}_2) \\ \vdots & \vdots & & \vdots \\ \chi_1(\tilde{r}_N) & \chi_2(\tilde{r}_N) & \cdots & \chi_N(\tilde{r}_N) \end{pmatrix} \tag{4}$$

A Slater determinant basis function satisfies the requisite anti-symmetry properties, and, since the spin orbitals are orthogonal, the set of $\binom{2M}{N}$ Slater determinant basis functions that can be formed from all subsets of size N with distinct elements from the $2M$ spin orbitals is an orthonormal set.

From a computational perspective, the FCI procedure consists of using a Rayleigh-Ritz method to approximate eigenfunctions and eigenvalues of (2). One starts with a collection of $K \leq \binom{2M}{N}$ orthonormal Slater determinant basis functions $\{v_j\}_{j=1}^{K}$ and seeks approximate eigenfunctions that are linear combinations of these functions;

$$\Psi \approx \sum_{j=1}^{K} c_j\, v_j \tag{5}$$

The coefficients of the approximate eigenfunctions are determined by finding the eigenvectors and eigenvalues of the finite dimensional linear system that is the projection of the operator H onto the subspace formed from the v_j's;

$$\tilde{\mathrm{H}}\vec{c} = \lambda \vec{c} \tag{6}$$

The (i,j)th entry of $\tilde{\mathrm{H}}$, $\tilde{\mathrm{H}}_{i,j}$, is given by

$$\tilde{\mathrm{H}}_{i,j} \;=< v_i\,, \mathrm{H}\, v_j > \tag{7}$$

The accuracy of the approximation is improved by expanding the number, M, of spin orbital basis functions, and, consequently, the number, K, of Slater determinant basis functions that can be formed from these spin orbitals.

3 Computational Procedures

A principal computational task associated with the FCI procedure, and with wave function based methods in general, is the evaluation of inner products involving Slater determinant basis functions, $< v_i\,, \mathrm{H}\, v_j >$. These inner products are integrals over the $3N$ spatial coordinates and the N spin coordinates of the N-particle wave function. However, as described in [19], since Slater determinant basis functions are linear combinations of products of spin orbitals, the task of evaluating these inner products can be reduced to the task of combining the results of the evaluation of integrals over R^3 and over R^6. The integrals over R^3 are known as "one-electron integrals" and have the form

$$\mathrm{I}_{(i,j)} = \int_{\mathrm{R}^3} \left[-\frac{1}{2}\,\phi_i(\vec{r})\,\Delta\,\phi_j(\vec{r}) \;-\; \sum_{\mathrm{A}=1}^{\mathrm{P}} \frac{Z_{\mathrm{A}}}{|\vec{r}-\vec{R}_A|}\,\phi_i(\vec{r})\,\phi_j(\vec{r}) \right] d\vec{r} \tag{8}$$

and must be evaluated for all $j \geq i$, $i = 1 \ldots M$, pairs of spatial orbital basis functions that are used to create the Slater determinant basis functions.

The integrals over R^6 are known as "two-electron integrals" and have the form

$$\mathrm{I}_{(i,j,k,l)} = \int_{\mathrm{R}^6} \frac{\phi_i(\vec{r})\,\phi_j(\vec{r})\,\phi_k(\vec{s})\,\phi_l(\vec{s})}{|\vec{r}-\vec{s}|}\,d\vec{r}\,d\vec{s} \tag{9}$$

These integrals are evaluated for all $j \geq i$, $i = 1 \ldots M$ pairs and all $l \geq k$, $k = 1 \ldots M$ pairs of spatial orbitals.

A challenge in the construction of grid based numerical methods is that of efficiently and accurately approximating the values of integrals of the form (8) and (9) when the spatial orbitals ϕ_i are discrete, e.g. they are grid based spatial orbitals.

For computational efficiency reasons we seek approximations that utilize a computational region that is rectangular and a grid that has a uniform mesh width in each direction. For the purposes of discussion, we assume that the mesh widths in each direction are equal and of size h. In practice, the mesh widths in each direction may be of unequal size, as long as the mesh width in each direction is uniform. With this choice of computational domain and grid, the approximations must be designed so that problems associated with the singularity of the integrand in (8) and (9) are avoided. In addition, the evaluation of the integrals in (9) must be done in such a way that avoids the direct evaluation of six dimensional integrals.

Both the one-electron and two-electron integrals require the approximation of integrals over the three dimensional computational domain. The integration formula used for the evaluation of these integrals is the standard multi-dimensional trapezoidal method. We assume that the spatial orbital basis functions vanish outside the computational domain so that the trapezoidal method will be just a simple weighted sum with uniform weights of function values over all mesh points

$$\int_{\mathrm{R}^3} f(\vec{r})g(\vec{r})d\vec{r} \;\approx \sum_i \sum_j \sum_k f_{i,j,k}\, g_{i,j,k}\, h^3 \tag{10}$$

For functions that are smooth and vanish at the boundaries, the trapezoidal method is "infinite order accurate", e.g. the rate of convergence behaves as h^p where the exponent p depends on the smoothness of the integrand [7].

3.1 One-electron Integrals

We first describe two methods for approximating the single particle integrals (8). In our approximation we assume that the spatial orbitals, ϕ_j, are known, are smooth functions that are well resolved by the computational grid, and vanish outside the computational domain. (The construction of a set of functions with these properties is described below). The integral (8) is the sum of two inner products, the first inner product requires the evaluation of $\phi_i(\vec{r})\,\Delta\,\phi_j(\vec{r})$. The Laplace operator in this term is approximated with standard high order centered finite differences. The results given in Section 4 utilize 6th order centered approximations and give quite satisfactory results. The values outside the computational domain that are required for the evaluation of the finite difference operator at points near the boundaries are taken to be identically zero; these values are consistent with the assumption that the spatial orbitals vanish outside the computational domain.

The more challenging approximation problem is that of approximating the second term in (8) because of the singularity of the integrand at the centers of the nuclei. The two methods we are proposing are distinguished by the type of approximation used to evaluate this integral. In the first method, the singular potential is replaced by a smoothed potential and then numerical integration performed. In the second, the integral is approximated by a high order interpolation of a solution of Laplace's equation in an infinite domain.

The first method is one that is motivated by the use of smooth kernels in vortex methods for incompressible fluid flow [1,9,10], and consists of applying the trapezoidal method to the approximation

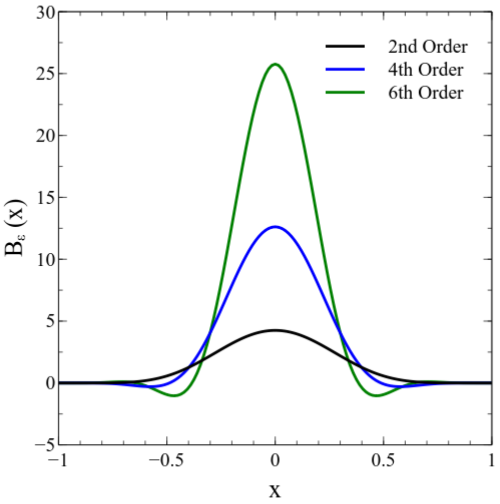
$$\int_{\mathrm{R}^3} \frac{\phi_i(r)\,\phi_j(r)}{|\vec{r}-\vec{R}_A|}\,d\vec{r} \approx 4\pi \int_{\mathrm{R}^3} \phi_i(r)\,\phi_j(r)\,\mathrm{G}_\epsilon(\vec{r}-\vec{R}_A)\,d\vec{r} \tag{11}$$

in which $\mathrm{G}_\epsilon(\vec{r}) = \dfrac{1}{4\pi|\vec{r}|} * B_\epsilon(r)$ is the mollified Green's function obtained by convolving the Laplace operator Green's function with the mollifier $B_\epsilon(r)$. To obtain high order rates of convergence with respect to the grid mesh size, the use of the trapezoidal method dictates that the mollifier be chosen so that $\mathrm{G}_\epsilon(\vec{r})$ has many continuous derivatives as possible. As is known from the error estimates for vortex methods [1,8,10], to improve the rate of convergence with respect to the mollification parameter ϵ, the mollifier B_ϵ should be chosen so that as many moments greater than the zeroth moment vanish. Lastly, the need to evaluate a large number of these integrals, each of which requires the sampling of the integrand at a large number of points, an analytic expression for $\mathrm{G}_\epsilon(\vec{r})$ is highly desirable. In our computational experiments, we make use of the family of mollifiers B_ϵ that are described in [4]. These mollifiers have the general form

$$B_\epsilon(r) = \begin{cases} \dfrac{\gamma_q}{4\pi\epsilon^3}\,(1-\left(\dfrac{r}{\epsilon}\right)^2)^q \left(1+\displaystyle\sum_{j=1}^{K-1}\alpha_j(1-\left(\dfrac{r}{\epsilon}\right)^2)^j\right) & r \le \epsilon \\ \\ 0 & r > \epsilon \end{cases} \tag{12}$$

The values of the coefficients in (12) are determined so that the mollifier has unit L^2 norm in R^3 and has order $2K$. (A mollifier is of order $2K$ if the mollifier has unit mass and all moments from order 1 to $2K$ vanish). The value of q in the mollifier determines its differentiability. For a given value of q, $B_\epsilon(r)$ is $q-1$ times continuously differentiable. The coefficients for mollifiers up to order 6 and up to 9 times continuously differentiable are given in [4]. Members of this family give rise to $\mathrm{G}_\epsilon(\vec{r})$'s that have analytic expressions.

Plots of mollifiers of order 2, 4 and 6 with $\epsilon = 1$ are given in Figure 1(a). The mollified Greens' functions, G_ϵ, associated with each of these mollifiers are shown in Figure 1(b) along with the exact Greens' function G. Since the mollifiers B_ϵ vanish outside $r=\epsilon$, the potential terms in (11) are only modified for values $r \le \epsilon$.



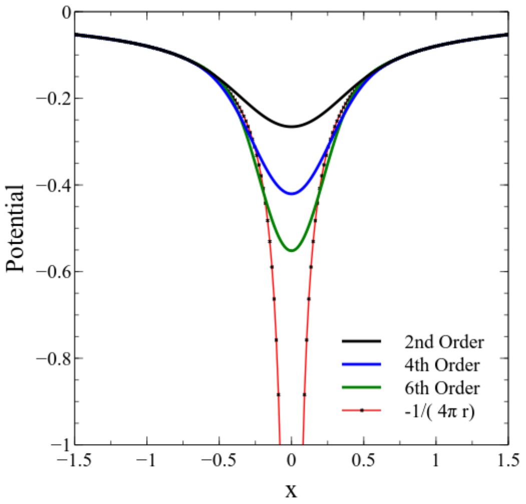


Figure 1(a)

$B_\epsilon(x)$ for $\epsilon = 1$

Figure 1(b)

$G_\epsilon(x)$ for $\epsilon = 1$

The second method we propose is based upon the observation that

$$\int_{\mathrm{R}^3} \frac{\phi_i(r)\,\phi_j(r)}{|\vec{r}-\vec{R}_A|} = \Phi_{i,j}(R_A) \tag{13}$$

where Φ satisfies

$$\Delta\Phi_{i,j} = -4\pi\,\phi_i\,\phi_j \qquad \text{for} \quad \vec{r} \in \mathrm{R}^3 \tag{14}$$

e.g. $\Phi_{i,j}$ is the solution of Laplace's equation with "infinite" boundary conditions. To obtain a value of the integral, one creates an approximate solution of (14) using a grid based method and then uses high order interpolation from the computational grid to obtain the value at R_A. If one were just computing single electron integrals, this second method requires substantially more work than the first method proposed, however, as will be discussed below, the solution of (14) using a grid based method is also needed for the evaluation of the two-electron integrals, and thus the cost of obtain the integral is just the cost of a local interpolation.

3.2 Two-electron Integrals

The method for computing double particle integrals is based on the observation that

$$\mathrm{I}_{(i,j,k,l)} = \int_{\mathrm{R}^6} \frac{\phi_i(\vec{r})\,\phi_j(\vec{r})\,\phi_k(\vec{s})\,\phi_l(\vec{s})}{|\vec{r}-\vec{s}|}\,d\vec{r}\,d\vec{s} = \int_{\mathrm{R}^3} \phi_k(\vec{s})\,\phi_l(\vec{s}) \int_{\mathrm{R}^3} \frac{\phi_i(\vec{r})\,\phi_j(\vec{r})}{|\vec{r}-\vec{s}|}\,d\vec{r}\,d\vec{s} \tag{15}$$

so that the evaluation of this six dimensional integral can be obtained as the product two three dimensional integrals. The computational procedure consists of a double for loop in which the outer loop consists of evaluations of integrals of the form

$$\Phi_{i,j}(s) = \int_{\mathrm{R}^3} \frac{\phi_i(\vec{r})\phi_j(\vec{r})}{|\vec{r}-\vec{s}\,|}\, d\vec{r} \tag{16}$$

at the nodes of the computational grid, and an inner loop where the complete integral is evaluated by forming trapezoidal approximation to the integral;

$$\mathrm{I}_{\,(i,j,k,l)} = \int_{\mathrm{R}^3} \Phi_{i,j}(s)\, \phi_k(\vec{s})\, \phi_l(\vec{s}) d\vec{s} \tag{17}$$

The primary computational difficulty in the evaluation of the two-electron integrals thus consists of evaluating (16). Instead of evaluating the integral directly for every point required for the trapezoidal approximation of the integral (17), we utilize the fact that the evaluation of the integral at every grid point can be obtained in one step by solving

$$\Delta\Phi_{i,j} = -4\pi\, \phi_i\, \phi_j \tag{18}$$

with "infinite" boundary conditions.

The need to evaluate the solution to Laplace equation with "infinite" boundary conditions is often required for the "field solve" step of particle-in-cell methods, and thus there are a variety of solution procedures that have been developed for this computational task [14, 16–18, 20]. However, these methods are typically optimized for highly localized sources, and since we assume that the spatial orbitals used to form the Slater determinant are not highly localized and are smooth, we were led to develop an "expanding domain" procedure that combines a spectral approximation of (18) with an analytic correction so that there is rapid convergence to the infinite domain limit as the computational domain is expanded [3, 5] The spectral discretization leads to very accurate solutions while computational efficiency is obtained through the use of high quality Fast Fourier Transform routines [12, 13].

3.3 Modified Bare Atomic Molecular Orbitals

The construction of an approximate solution of the N-particle Schroedinger equation using Slater determinant basis functions requires a specification of a set spatial orbitals. One's desire to use a uniform grid and spectral approximations dictates that the basis functions be as smooth (differentiable) as possible. With the use of a computational grid, there is great flexibility in selecting basis functions, and in this section we describe a method for creating sets of orbitals that are both smooth and adaptive in the sense that they are dependent upon the configuration of the nuclei participating in the computation. Other procedures for constructing smooth orbitals are certainly possible, e.g. smooth locally centered atomic orbitals such as those described in [6].

The procedure we propose is an extension of the idea behind the use of the cryogenic orbitals commonly used in the description of atomic structure. Specifically, for a single atom the hydrogenic orbitals are eigenfunctions of the operator

$$-\frac{1}{2}\Delta - \frac{Z}{|\vec{r}\,|} \tag{19}$$

An obvious extension to multiple atoms are the use of spatial orbitals that are the eigenfunctions of the operator

$$-\frac{1}{2}\Delta - \sum_{\mathrm{A}=1}^{\mathrm{P}} \frac{Z_{\mathrm{A}}}{|\vec{r} - \vec{r}_{\mathrm{A}}|} \tag{20}$$

e.g. the eigenfunctions of the separable part of the full Hamiltonian (2). Since the latter eigenfunctions are eigenfunctions in which electron-electron interactions are absent, we refer to these orbitals as "Bare Atomic Molecular Orbitals" (BAMO's). One attractive feature of these orbitals is that they are immediately orthonormal and naturally adapt themselves to different atomic configurations.

The unattractive features of these orbitals is that they are not known analytically and must be computed, they have non-smoothness that is introduced due to the singularity in the nuclear potential and they have infinite extent. One cannot avoid their numerical construction, but one positive aspect of determining the orbitals numerically is that it is relatively easy to insert modifications to the operator so that the resulting eigenfunctions have desirable smoothness and boundedness properties. In particular, instead of creating eigenfunctions of (20), we create and use smooth Bare Atomic Molecular Orbitals that are the discrete eigenfunctions of an approximation to the operator (20) by an operator with a mollified nuclear potential, $\mathrm{G}_\epsilon(\vec{r})$, a variable reciprocal mass coefficient, $a_\gamma(\vec{r})$, and a domain boundary potential, $\Phi_b(\vec{r})$,

$$-\frac{1}{2}\nabla \cdot (a_\epsilon(r)\nabla) - \sum_{\mathrm{A}=1}^{\mathrm{P}} Z_{\mathrm{A}}\, \mathrm{G}_\epsilon(\vec{r} - \vec{R}_A) \; + \; \Phi_b(\vec{r}) \tag{21}$$

In this operator, the mollified nuclear potential is a potential of the same construction as that used for the approximation of the single particle operators (11). As indicated by the results in [6] in which an operator with modifications similar to those in (21) is used to create smooth discrete orbitals for a single atom, the use of a high order mollifier is extremely beneficial. Moreover,the size of the smoothing parameter needed to obtain "chemical accuracy (e.g. .001 Hartrees) in the eigenvalues is not excessively small.

The reciprocal mass coefficient and the boundary potential are selected so that the eigenfunctions corresponding to some number of the lowest eigenvalues vanish as the boundary of the computational domain is approached. To accomplish this, the reciprocal mass coefficient $a_\gamma(r)$ is a function that is identically equal to one in the interior of the computational domain and transitions to zero over the region of width γ near the computational boundary. The boundary potential is a potential that is identically zero in the interior of the computational domain, but transitions to a large positive value over the region that the reciprocal mass tends to zero. Since the reciprocal mass coefficient vanishes on the computational boundaries, at boundary points the operator (21) is a scalar operator whose eigenfunctions are discrete delta functions located at the boundary points with eigenvalues given by the sum of the nuclear potential and the boundary potential evaluated on the boundary. As long as the value of this sum is greater than the upper bound for the eigenvalues of the desired eigenfunctions, the orthogonality of all eigenfunctions insures that the desired eigenfunctions will vanish on the domain boundaries.

4 Determination of Computational Parameters and Sample Results

In this section we give an example that demonstrates how the computational procedures described above can be combined to obtain approximate solutions of the N-particle Schroedinger atom using a completely grid based FCI procedure. The dissociation of H_2 was chosen as an example because it is perhaps the simplest example that involves more than a single atom and one for which very accurate numerical solutions have been previously published [15]. In addition, there is some independent interest in the investigation of the rapidity with which solutions obtained with Slater determinants constructed using modified BAMO's converge to the two particle eigenfunctions.

In this example, the nuclei are located at R_A and R_B, and seek approximate eigenvalues and anti-symmetric eigenfunctions of

$$\left(-\frac{1}{2}\nabla_a^2 - \sum_{S=A,B} \frac{1}{|r_a - R_S|} - \frac{1}{2}\nabla_b^2 - \sum_{S=A,B} \frac{1}{|r_b - R_S|} + \frac{1}{|r_a - r_b|}\right)\Psi = \lambda\Psi$$

as $D = R_A - R_B$ varies. The procedure for specific values of R_A and R_B consists of

(i) Determining the values of the numerical parameters that lead to results with acceptable accuracy.

(ii) Compute modified Bare Atomic Molecular Orbitals by finding the lowest M eigenfunctions of (20)

(iii) Evaluate all one-electron and two-electron integrals associated with the M orbitals.

(iv) Assemble the discrete Hamiltonian matrix using the one-electron and two-electron integral data.

(v) Determine the smallest eigenvalue and eigenvector of the discrete Hamiltonian matrix.

Since many of the eigenvalues and eigenvectors associated with the finite dimensional Hamiltonian of the FCI approximation, as well as the discrete approximation of (21) are degenerate, the use of a robust iterative method for determining the eigenpairs was necessary. The particular iterative method used to obtain the results presented here was the Rayleigh-Chebyshev method described in [2]. The stopping tolerance used was sufficient to obtain eigenvalue approximations that were converged to approximately five digits.

4.1 Numerical Parameter Determination

In order to determine the values of the numerical parameters, one must distinguish between two types of errors that are associated with the computational procedure. The first type of error, the"numerical discretization error", is the error associated with implementing the constituent operations required to set up and solve the equations arising from an FCI approximation using a specified orbital basis set as well as the errors associated with constructing an orbital basis set if it is determined computationally. The other type of error, the "orbital basis set error", is the error due to approximating the desired eigenfunctions by a linear combination of Slater determinants that are formed from a specified set of spatial orbitals. Our main interest in presenting the computational example is to demonstrate discretization procedures that enable one to reduce the discretization error to sufficiently small values so that one can reliably investigate orbital basis set errors.

Numerical parameters for the FCI equation construction

For a given orbital basis set whose elements are assumed to vanish outside the computational domain, several numerical parameters influence the errors associated with setting up and solving the equations arising from an FCI approximation. These parameters are the mesh size, the order of accuracy of the finite difference approximation to the second derivative operator in (8), the parameters associated with the "infinite" domain solutions of Laplace's equation, and, depending whether one uses (11) or (13) to evaluate the nuclear potential term in the single electron integral, the parameters associated with the use of a smoothed Green's function or the parameters associated with interpolation from a grid to nuclear centers. To achieve accurate results with as large mesh sizes as possible, we used sixth order centered difference approximations for the discrete approximation to the Laplacian in (8). Parameters were chosen for the method described in [3,5] for the solution of Laplace's equation in infinite domains that resulted in solutions that converged with 8th order accuracy with respect to the spatial discretization. The domain size expansion factor parameter η was fixed at 2.0, a value sufficiently large so that the changes in the solutions obtained with this value were less than 1×10^{-4} in absolute magnitude. The smoothing function used to create the mollified Green's function required in (11) was sixth order and six times continuously differentiable. When (13) was used to determine the nuclear potential contribution to the single orbital integrals, a sixth order polynomial interpolation formula was used. Lastly, the trapezoidal method is used for integrals over the computational domain. Since all the integrands vanish outside of the computational domain, this approximation is spectrally accurate.

The specific values of the two remaining parameters, the mesh size and the size of the mollifier parameter ϵ, that are required to obtain accurate approximations depends upon the elements of the orbital basis set one is using. If one uses an orbital basis sets whose elements are known analytically, then one typically determines the mesh size by carrying out convergence studies and selects a mesh size sufficiently small so that further reductions in mesh size lead to changes in the computational results that are less than some target tolerance. When one is using (11) and convergent results are obtained in the double limit of the mesh size tending to zero and $\epsilon \to 0$, we found it useful to sweep through a collection of values of ϵ, and for each value of ϵ determine a mesh size that lead to convergent results. The value of ϵ used was then chosen to be that value for which further reductions in ϵ leads to changes in the results that are below a target tolerance.

For the results presented here, we used a computationally determined orbital basis where the type of discrete approximations to the operators used in the basis set construction are identical to those used for the construction of the FCI equations. Because of the identical nature of the discrete approximations, the values of the mesh size and the smoothing parameter ϵ where chosen to be identical to those values that lead to the determination of sufficiently converged approximations of the eigenvalues and eigenvectors of (21) as described below.

Numerical parameters for modified BAMO basis construction

In order to achieve accurate and sufficiently converged approximations to the eigenvalues and eigenfunctions of (21) with a large a mesh size as possible, sixth order finite difference approximations were used to approximate the differential operator, and six times continuously differentiable functions as described in [4] were used for both for the smoothed Green's function approximation of the nuclear potential. The far-field boundary transition function was the product of one-dimensional smooth "top-hat" functions in which the boundary transition function was a smooth step function obtained by integrating the fifth order one dimensional polynomial mollifier given in [4].

The determination of the transition distance γ, the size of the smoothing parameter ϵ, and the mesh size necessary to obtain sufficiently converged results, was a bit more challenging and required developing a systematic approach. Specifically, we first determined the the number of grid panels per atomic unit that were necessary to obtain converged eigenvalues for computations where the far-field boundary condition transition distance was fixed at $\gamma = 1.5$. To determine this value, the computation of the eigenvalues of (21) on a test problems with no nuclear charge was carried out. These computations were carried out on a small domain, $\Omega = [-3, 3]^3$, since we were only interested in observing convergence behavior and not concerned with the specific values to which the eigenvalues are converging. The results are given in Table 1. The value E_0^* is the value of the lowest eigenvalue obtained with 20 panels/a.u (a value that differed from a computation with 22 panels/a.u by less than 1×10^{-9}).

Panels/a.u.	4	5	6	7	8	10
E_0	6.1590e-01	6.4426e-01	6.4761e-01	6.4796e-01	6.4799e-01	6.4800e-01
$\|\|E_0 - E_0^*\|\|$	3.2103e-02	3.7395e-03	3.9109e-04	3.5409e-05	4.2822e-06	9.1396e-07

Table 1: Convergence of lowest eigenvalue of (21) with panels/a.u. $\Omega = [-3, 3]^3$, $Z_1 = 0$, $\gamma = 1.5$

The conclusion drawn from these results is that with a smoothing transition width of $\gamma = 1.5$, fluctuations in the computed eigenvalues will be less than 5×10^{-4} as long as the the number of panels/a.u. used is greater than 6.

The next step was the determination of the size of ϵ required to determine sufficiently converged approximations to the lowest eigenvalue when $\epsilon = 0$. This value was determined by carrying out a sequence of approximations to the lowest eigenvalue of (21) with a single nuclear charge located at the non-grid point location (0.012, 0.12, -0.1). The number of panels/a.u. was 16. The results are shown in Table 2.

ϵ	.2	.3	.4	.5	.6	.7	.8	.9	1.0
E_0	-0.3841	-0.3840	-0.3838	-0.3835	-0.3830	-0.3824	-0.3816	-0.3806	-0.3794

Table 2: Convergence of lowest eigenvalue of (21) with size of mollification parameter ϵ. $\Omega = [-3, 3]^3$, $Z_1 = 1.0$, $\gamma = 1.5$

From these results, we concluded that using a value of $\epsilon = 0.5$ would be sufficient to determine an approximate eigenvalue with a precision of better than 1.0×10^{-3}. With this value of ϵ, a further set of convergence studies were carried out to determine the number of panels/$a.u.$ required to obtain sufficiency converged results for this value of ϵ. The results of this latter study are presented in Table 3.

Panels/a.u.	4	5	6	7	8	10
E_0	-3.9172e-01	-3.8438e-01	-3.8377e-01	-3.8358e-01	3.8352e-01	-3.8349e-01
$\|\|E_0 - E_0^*\|\|$	8.2456e-03	9.0288e-04	2.9244e-04	1.0831e-04	4.6449e-05	1.2581e-05

Table 3: Convergence of lowest eigenvalue of (21). $\Omega = [-3, 3]^3$, $Z_1 = 1.0$, $\epsilon = 0.5$, and $\gamma = 1.5$

The value of E_0^* used in Table 3 is the value obtained with 16 panels/a.u. Based upon these results, we concluded that for a nuclear charge smoothing of size $\epsilon = 0.5$, using a number of panels/a.u. greater than 6 was sufficient to obtain a lowest eigenvalue approximation with a precision of better than 1.0×10^{-3}.

Additional modified BAMO basis parameters

In addition to determining the appropriate numerical parameters to be used for the construction of the eigenfunctions and eigenvalues of (21), one must specify the computational domain dimensions. Since the computational domain specification implicitly determines the support of the functions in the orbital basis set, the domain specified must be large enough to contain (or very nearly contain) the support of wave function density associated with the state that one seeks to approximate. This test problem is concerned with the ground state energies of H_2 as it is dissociated and so we specified the computational domain as the bounding box of two cubic regions, each cubic region centered about a hydrogen nucleus. The size of each cubic region was chosen so that a ground state energy of the single hydrogen atom located at it's center could be computed with an error of approximately $.001eV$. In the computational results described below, the width of the computational cube about each nucleus was chosen to be $12a.u.$, and thus the computational domain boundaries were always greater than $6a.u.$ away from the nuclear centers.

4.2 Dissociation of H_2

With a specification of the values of numerical parameters required to obtain sufficiently converged results for the discrete approximations used, the computational task then becomes one of carrying out the steps (ii)-(v) for different numbers of elements in the orbital basis set and different separation distances between the two hydrogen nuclei. Of particular interest is the assessment of the orbital basis set errors when one uses a modified BAMO basis set. To assess this error, we computed approximate solutions with an increasing number of orbital basis elements for range of separation distances from 2 to 8. The accuracy of the resulting approximation was estimated by comparing the our results to those given in [15] (e.g. the values of the “exact” solution are the values obtained with an approximation procedures specifically designed for the evaluation of the states of H_2.)

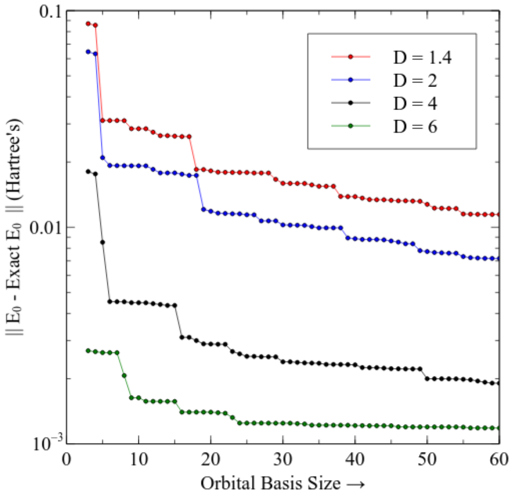


Figure 2

Convergence with respect to orbital basis set size.

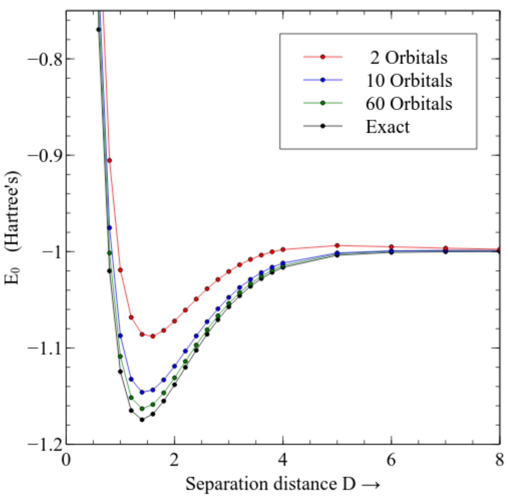


Figure 3

Ground state energy as a function of separation distance

In Figure 2 we present the convergence behavior of the ground state energy with respect to numbers of basis elements for several different values of the separation distance. For large values of separation, where the computation is essentially that associated with two independent hydrogen atoms, the error saturates quickly to the accuracy associated with the use of a finite difference procedure and a smoothed orbital basis approximation. For closer values of separation, the errors are dominated by the size of the orbital basis set. Convergence is observed, and is strictly monotone when one increments the basis set using each of the subspaces associated with a given eigenvalue. Also, for a wide range of separation distances, the number of orbital basis set elements required to obtain a particular accuracy is nearly constant, a fact that strongly indicates the adaptive nature of the modified BAMO basis sets.

In Figure 3 we show plots of the ground state energy verses separation distances when using several fixed numbers of orbital basis set elements. We note that there is qualitative agreement with the “exact” results even for a minimal basis set consisting of two orbitals, and that with this particular basis and ten orbital basis elements the relative error of the minimal energy to be less than 2.5%.

Since the size of the errors associated with the numerical approximations can be expected to be on the order of the errors associated with large separation distance, e.g. less than .001 Hartrees, the errors observed at smaller separation distances which are on the order of .1 Hartrees can be assumed to be due to orbital basis set error. Thus, the computational results can be used to deduce that the modified BAMO's have decreasing effectiveness as one includes elements with larger and larger eigenvalues. This behavior is not entirely unexpected, as the members of the orbital basis set with larger eigenvalues tend to Fourier modes and are not localized. We presume that the ineffectiveness of the basis set for large eigenvalues is due to the fact that the ground state wave function possesses localized features that require many Fourier modes to capture.

5 Conclusion

This paper is concerned with describing how a collection of discretization techniques can be combined to create a method for the determination of approximate wave functions of the N-particle Schroedinger equation. In this method, both high order finite difference and spectral approximations of differential and integral operators are used to obtain high accuracy. In order to obtain the rapid rates of convergence with respect to mesh size that are made possible with this type of discretization it is necessary that the singular nature of the nuclear potential be handled appropriately. In the method proposed here, the singular potential is accommodated through the use of mollified potentials that are obtained by convolution with high-order approximate delta functions [4]. In addition, the primary computational task associated with the evaluation of the one and two-electron integrals is reduced to that of evaluating the solution of Poisson's equation in an infinite domain. The procedure used here for obtaining this solution is the "expanding domain" procedure described in [3, 5]. High computational efficiency of the latter procedures is obtained using a uniform rectangular grid and high performance fast Fourier transform routines [12, 13].

If supplied with analytic or a pre-determined set of spatial orbitals, one can utilize the discretization methods presented here to create accurate approximations of the matrix elements associated with the Full Configuration Interaction (FCI) procedure. The use of completely grid based approximations provides the opportunity to utilize numerically determined orbital basis functions. As a demonstration of this capability, we proposed and and then demonstrated the use of a collection of orbitals that are the approximations to the eigenfunctions of a single particle operator in the presence of bare nuclei, the bare atomic molecular orbitals (BAMO's).

One of the difficulties of using the discretization methods described here is the determination of appropriate values of their constituent numerical parameters, in particular the appropriate mesh width size and size of the smoothing parameter used for creating the mollified potential. However, as described in the computational results section, appropriate parameter values can be identified through the investigation of the convergence behavior of the numerical procedures on a collection of simplified test problems.

Computational results on the use of numerically computed BAMO basis sets demonstrated that completely grid based discretizations can be used to create approximation solutions of the N-particle Schroedinger equation with an error that is less than the orbital basis set errors. In particular, the procedure was used to carry out a preliminary investigation of the effectiveness of the BAMO's as an adaptive basis set for the dissociation of H_2. It was observed that BAMO orbitals associated with the smallest eigenvalues provide a very good initial approximation, but their effectiveness with increasing number decreases rapidly. This conclusion leads to an obvious application of the procedures proposed here, namely, the investigation and development of procedures for creating numerically determined basis sets with improved convergence properties.

Bibliography

[1] Christopher Anderson and Claude Greengard. On vortex methods. *SIAM J. Numer. Anal.*, 22(3):413–440, 1985.

[2] Christopher R. Anderson. A Rayleigh-Chebyshev Procedure for Finding the Smallest Eigenvalues and Associated Eigenvectors of Large Sparse Hermitian Matrices. *J. Comput. Phys.*, 229(19):7477–7487, September 2010.

[3] Christopher R. Anderson. A Recursive Expanding Domain Method for the Solution of Laplace's Equation In Infinite Domains. Technical Report CAM-14-45, Department of Mathematics, UCLA, Los Angeles, California, May 2014.

[4] Christopher R. Anderson. Compact Polynomial Mollifiers For Poisson's Equation. Technical Report CAM-14-43, Department of Mathematics, UCLA, Los Angeles, California, May 2014.

[5] Christopher R. Anderson. High Order Expanding Domain Methods for the Solution of Laplace's Equation In Infinite Domains. Technical Report CAM-14-44, Department of Mathematics, UCLA, Los Angeles, California, May 2014.

[6] Christopher R. Anderson. Uniform Grid Computation of Smooth Hydrogenic Orbitals. Technical Report CAM-15-09, Department of Mathematics, UCLA, Los Angeles, California, February 2015.

[7] K.E. Atkinson. *An Introduction To Numerical Analysis.* Wiley, 2nd edition, 1978.

[8] J Thomas Beale and Andrew Majda. High order accurate vortex methods with explicit velocity kernels. *Journal of Computational Physics*, 58(2):188–208, 1985.

[9] Alexandre Joel Chorin. Numerical study of slightly viscous flow. *Journal of Fluid Mechanics*, 57:pp 785–796, 1973.

[10] G-H Cottet and P D Koumoutsakos. Vortex Methods: Theory and Practice. *Measurement Science and Technology*, 12(3):354, 2001.

[11] Jean-Luc Fattebert and Marco Buongiorno Nardelli. Finite Difference Methods for Ab Initio Electronic Structure and Quantum Transport Calculations of Nanostructures. In C. Le Bris, editor, *Handbook of Numerical Analysis, Volume X: Special Volume: Computational Chemistry.* Elsevier Science, 2003.

[12] Matteo Frigo and Steven G. Johnson. The Design and Implementation of FFTW3. *Proceedings of the IEEE*, 93(2):216–231, 2005. Special issue on “Program Generation, Optimization, and Platform Adaptation”.

[13] Matteo Frigo and Steven G. Johnson. FFTW 3.3.4. http://www.fftw.org/, 2014.

[14] R.A James. The solution of poisson’s equation for isolated source distributions. *Journal of Computational Physics*, 25(2):71–93, 1977.

[15] Wl/odzimierz Kol/os, Krzysztof Szalewicz, and Hendrik J. Monkhorst. New Born–Oppenheimer potential energy curve and vibrational energies for the electronic ground state of the hydrogen molecule. *The Journal of Chemical Physics*, 84(6):3278–3283, 1986.

[16] P. McCorquodale, P. Colella, G.T. Balls, and S.B. Baden. A scalable parallel Poisson solver in three dimensions with infinite-domain boundary conditions. *International Conference Workshops on Parallel Processing, ICPP 2005 Workshops*, pages 163–172, 2005.

[17] Peter McCorquodale, Phillip Colella, Gregory T. Balls, and Scott B. Baden. A local corrections algorithm for solving Poisson’s equation in three dimensions. 2:57–81, 2007.

[18] D.B. Serafini, P. McCorquodale, and P. Colella. Advanced 3D Poisson solvers and particle-in-cell methods for accelerator modeling. *Journal of Physics: Conference Series*, 16(1):481–485, 2005. cited By (since 1996)2.

[19] A. Szabo and N.S. Ostlund. *Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory*. Dover Books on Chemistry Series. Dover Publications, 1996.

[20] Z Jane Wang. Efficient implementation of the exact numerical far field boundary condition for Poisson equation on an infinite domain. *Journal of Computational Physics*, 153(2):666–670, 1999.