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Spectrally accurate numerical solution of the single-particle Schrödinger equation

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We have formulated a three-dimensional fully numerical (i.e., chemical basis-set free) method and applied it to the solution of the single-particle Schrödinger equation. The numerical method combines the rapid ''*exponential*'' convergence rates of spectral methods with the geometric flexibility of finite-element methods and can be viewed as an extension of the spectral element method. Singularities associated with multicenter systems are efficiently integrated by a Duffy transformation and the discrete operator is formulated by a variational statement. The method is applicable to molecular modeling for quantum chemical calculations on polyatomic systems. The complete system is shown to be efficiently inverted by the preconditioned conjugate gradient method and exponential convergence rates in numerical approximations are demonstrated for suitable benchmark problems including the hydrogenlike orbitals of nitrogen. [S1050-2947(98)04006-2]

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I. INTRODUCTION

The primary computational tool for *ab initio* quantum chemical calculations has focused around the linear combination of atomic orbitals (LCAO) method and its need to derive, often exotic, chemical basis sets. Recent efforts have attempted to remove the need to employ these chemical basis sets by developing a more local characterization of the solution via methods such as finite elements and finite differences. These methods remove the need to derive the global chemical basis sets for a specified problem by employing universal approximations at local regions in physical space. For multicenter systems the potential fields are characterized by Coulomb repulsive terms that contain r^{-1} type singularities at the nuclei locations in a three-dimensional space and the operator's potential field are given as a function of the molecular orbitals themselves, Eq. (1). Up to this point the local space, fully numerical, methods have only been applied to atomic and diatomic problems where coordinate transforms can remove the singularities associated with the Schrödinger type operators. Here a three-dimensional fully numerical (i.e., chemical basis-set free) method is formulated and applied to the solution of such operators,

$$\left[\frac{1}{2}\nabla^2+\frac{Z}{r}+V(\mathbf{x})\right]\phi_i(\mathbf{x})=\varepsilon_i\phi_i(\mathbf{x}) \quad \text{in} \quad \Omega^3, \tag{1}$$

where $r^2=x^2+y^2+z^2$, $V(\mathbf{x})$ is the external potential field, and Z is a constant. The numerical method combines the rapid ''*exponential*'' convergence rates of spectral methods with the geometric flexibility of finite-element methods and can be viewed as an extension of the spectral element method [1–3]. Multicenter problems of arbitrary geometry and number of nuclei are easily dealt with by the numerical method discussed here. A variational formulation is applied to the operator and the singularity is efficiently captured by an integral transformation. The physical space domain is decomposed into six pyramids around each singularity and patched to quadrilaterals in the remaining domain. Within each pyramid the solution is decomposed into either a warp product form of selected Jacobi polynomials [4], or Lagrangian interpolants in the mapped space. The solution within each quadrilateral is decomposed into a tensor product form of Lagrangian interpolants, as done in the spectral element method. In the case of the warped product form the matching of the pyramid and quadrilateral approximations is done by an interfacial variational statement that ensures overall convergence; for the Lagrangian interpolants in the mapped space a C^0 constraint is routinely applied. The global variational formulation preserves the symmetry of the operator and allows efficient inversion by preconditioned conjugate gradient methods. In addition, the formulation of the variational statement and integral transformation for the singularity produces a method that can effectively deal with singularities as high as r^{-p}, $p<3$, in three dimensions.

Traditional methods for solving Eq. (1) in solid-state applications involve the use of plane-wave basis and pseudopotentials that tend to bypass the singularity and yield significantly degraded convergence rates for the approximation [5]. For applications to molecular chemistry the linear combination of atomic orbitals, LCAO, method is traditionally used, where Gaussian basis sets, and their modifications, are the preferred global basis set. Issues involving singular integrals are done analytically [6] for these basis sets. However, the LCAO method suffers from slow ''algebraic'' convergence with respect to the size of the basis set. Furthermore, the construction of a global chemical basis set has evolved into as much as an art as a science and much effort is focused on developing appropriate chemical basis sets for a specific molecular structure. In the context of the LCAO method a pseudospectral method has been applied to electronic structure calculations [7]. The use of collocation has been shown to have advantages with regards to the computational complexity of the multi-centered integrals however it still suffers from the drawbacks of slow convergence of the expansion and optimal choice for a basis set. Here a somewhat universal basis set is adopted in a local region of physical space and rapid convergence is guaranteed in terms of size of the expansion. The method is also readily applied to both applications in solid state physics and molecular chemistry with geometrically complex nuclei distributions [8]. Attempts in the past to use finite-element methods [9–12] have either dealt only with atomic or diatomic molecules, where the singularity can be removed through a spherical or prolate spheroidal coordinate system, or through a costly use of the Fourier transform of r^{-1}. However, the advantages in using local methods versus global expansions has been recognized by these previous studies. These include advantages in computational scalings to large molecules and improved accuracy of spatial moments, $\langle r^p \rangle$, and gradients. Applications of local methods to multicenter systems have been addressed in [13] where each nuclei is treated as a separate solution with its own spherical coordinate system and the individual solutions are added together by a somewhat arbitrary weighting function. The individual treatment of nuclei and subsequent addition has obvious disadvantages in scalings to large numbers of nuclei and is avoided by the present method.

Here the singularity is dealt with in a systematic fashion and numerical errors are a direct consequence of the degree of the polynomial used within the local domain as well as the physical size of the local pyramid domains. This geometric flexibility is of particular interest for applications that have solutions that are highly localized near the nuclei locations and that may exhibit large gradients there. The method presented here has the geometric flexibility to deal with both solutions that are localized near the nuclei and those that have a more diffuse character throughout the molecule. A heuristically optimal domain decomposition that is somewhat locally spherically symmetric around the nuclei and diffuse at far field regions is, in some sense, natural to the formulation.

The formulation of the integral transformation and local space approximation are given in Sec. II for the solution of Eq. (1). First the spectral element method is briefly discussed and two formulations are presented that lead to numerical algorithms that efficiently integrate and approximate the singularity term. The resulting algebraic systems are presented and inversion methods are discussed for the numerical solution. In Sec. III results are presented from chosen benchmark calculations for the solution of Eq. (1). Solutions of Eq. (1) are presented for $V(\mathbf{x})=0$ and various different asymptotic behaviors near the singularity. Exponential convergence rates are demonstrated for solutions with zero and nonzero values at the location of the point singularity in a cubic domain. The hydrogenlike orbitals of nitrogen are also calculated to demonstrate applications to infinite domains with cusps at the nuclei locations. The method is expected to yield significant advances for accurate and robust all electron calculations within the context of molecular orbital theory and particularly density functional theories.

II. FORMULATION

A. Spectral element method

The spectral element method is designed to solve elliptic boundary value problems in general complex domains by partitioning the given domain into quadrilaterals, i.e., spectral elements. Within each element the solution is approximated by a Lagrangian interpolant basis, where tensor product forms are used in multidimensions. The first step in the procedure is to employ a variational formulation of the problem,

$$\frac{1}{2}\int_{\Omega_k} \nabla U(\mathbf{x})\cdot\nabla\phi(\mathbf{x})d\mathbf{x} - \int_{\Omega_k}\left(\frac{Z}{r}+V(\mathbf{x})\right)U(\mathbf{x})\phi(\mathbf{x})d\mathbf{x} = -\int_{\Omega_k} U(\mathbf{x})f(\mathbf{x})d\mathbf{x}, \tag{2}$$

where $U(\mathbf{x})$ is the chosen test function and $f(\mathbf{x})$ is a forcing function, $\varepsilon_i\phi_i$ in Eq. (1). Next the interpolation points are chosen to define a basis set via the Lagrangian interpolants; in the standard spectral element formulation Gauss-Lobatto Legendre (GLL) points are chosen. The solution is expanded in terms of high-order polynomial interpolants, $h_i(\xi)$, within a cube that are related to the physical space subdomain through an isoparameteric mapping for deformed elements, Eq. (3).

$$\phi(\eta,\xi,\zeta)=\phi_{ijk}h_i(\eta)h_j(\xi)h_k(\zeta) \tag{3}$$

The test functions are also chosen as the interpolants, as in the traditional Galerkin formulation. In the case of deformed geometries the boundary is also expanded in GLL interpolants. Lastly, the type of numerical quadrature must be chosen. The logical choice is GLL quadrature to coincide with the interpolation points; therefore the interpolants are defined by $h_i(\xi_j)=\delta_{ij}$; this gives the method a collocation type character. This choice of quadrature points and basis sets forms a discrete system of algebraic equations with a large degree of sparseness [1–3]. Standard Galerkin error estimates for the Laplacian predict

$$\|\phi-\phi^h\|_m \leqslant ch^{\alpha}\|\phi\|_r,$$

where $\alpha=\min(N+1-m,r-m)$, N is the polynomial degree appearing in the basis functions, and h is a parameter related to the element size. The exponential convergence property, associated with polynomials from the singular Sturm-Liouville operators [14] gives the method a significant advantage over traditional finite element and finite difference methods. In large scale applications several orders of magnitude less grid points are needed for the same accuracy when compared to traditional low-order methods; and if needed highly accurate solutions can be obtained at relatively little cost. The spectral element method has been used in three-dimensional solutions of fluid flow as well as large scale solutions of eigensystems of coupled partial differential equations [15–17].

Although the spectral element method has proven to be a useful technique for the above applications; there are a number of obstacles that must be overcome in order to apply such a method to Schrödinger-type operators and electronic structure computations. First, the presence of cusps at the singularity locations destroys the smoothness of the solution within the domain and the exponential convergence is lost. The discontinuity of the first derivative is likely to produce large oscillation in the regions of the singularity, a Gibbs phenomenon. Second, the presence of the r^{-1} singularity cannot be dealt with since the potential field must be finite at a given integration point due to the collocation character of the method. Lastly, the use of Gaussian quadrature for numerical integration does not converge for integrands with end-point singularities of r^{-1} or higher [18].

B. Molecular spectral element

The molecular spectral element method (MSE) is formulated to deal with the numerical difficulties of a finite number of arbitrary spaced cusps and point singularities. The combination of geometric flexibility and exponential convergence rates yields a well suited technique for solving Schrödinger-type operators. The first obstacle is the elimination of the Gibbs phenomenon associated with discontinuous derivatives at the singularity locations. The traditional spectral element method is basically capable of dealing with point cusps if the location is known *a priori*. By placing the corner of a given element at the singularity location the combination of the piecewise variational statement and the imposition of only a C^0 continuity constraint will allow the cusps to be accurately approximated. Convergence to the discontinuous derivative will be automatically met by the convergence of the method since within each elemental domain the solution is smooth. The second obstacle is numerical integration of the r^{-1} singularity. At first glance it may be suggested that the integration scheme be changed to a Gauss-Radau versus the Gauss-Lobatto quadrature used above. This eliminates the infinite potential value at an integration point since Gauss-Radau only uses one end point as an integration point. For solutions that decay to zero at the singularity location this adjustment does in fact work; however, this does not solve the problem that in general Gaussian quadrature does not converge for end-point singularities, of this order or higher, when solutions have nonzero values at the singularity location. This is of particular importance in electronic structure computations since several eigenfunctions will have nonzero values, e.g., atomic s-type orbitals; and in general their location in the spectrum is not known *a priori*.

The integration must be incorporated into the general method without any knowledge of the type of solution that exists. This can be effectively handled by an integral transformation proposed by Duffy [19]. Duffy proposed the integration of vertex singularities by subdividing a cube into square based pyramids and used the transformation $y=xu$ and $z=xw$. This reduces the integration over a pyramid

$$\int_0^1 dx \int_{-x}^{x} dy \int_{-x}^{x} dz\, r^{-1}\phi(x,y,z) \quad \text{in } \Omega^3 \tag{4}$$

to the evaluation of integrals of the form

$$\int_0^1 dx \int_{-1}^{1} du \int_{-1}^{1} dw\, \frac{x\phi(x,xu,xw)}{\sqrt{1+u^2+w^2}} \quad \text{in } \Omega^3. \tag{5}$$

Thus we partition the volume around the singularity with a cube and subdivide the cube into six pyramids, see Fig. 1. The transformation removes the singularity and smooth integrands remain that can be efficiently integrated with product Gauss quadratures. This type of domain decomposition is somewhat optimal for solutions that are asymptotically spherically symmetric around the singularity and tends to reduce the number of elements needed to fill the remaining domain substantially.

The last aspect in the formulation is an efficient approximation scheme for the transformed function $\phi(x,xu,xw)$. The use of Gauss-type quadrature over the cubic domain in the mapped space (x,u,w) leads to integration points that can be used to form Lagrangian interpolants in a similar fashion as is done in a traditional spectral element scheme, $\phi(x,xu,xw)=\phi_{ijk}h_i(x)h_j(y)h_k(z)$. However, this would require additional interpolation in the final formulation and was found to lead to a poorly conditioned numerical system to invert. A second approximation scheme is to expand the function into Lagrangian interpolants in the mapped space $\phi(x,xu,xw)=\phi_{ijk}h_i(x)h_j(u)h_k(w)$ and formulate appropriate operator transformations. Yet, a third method of approximation is a warp product representation of the solution [4] and was chosen as a suitable choice in [20] for nonsingular operators, see Eq. (6).

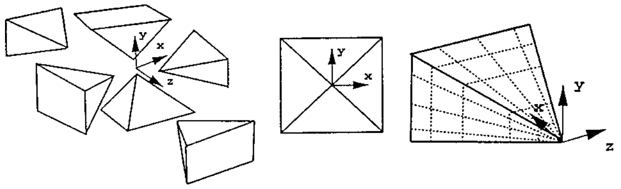

FIG. 1. Illustration of the pyramid decomposition of a cubic region around the singularity. The solutions within the pyramids are represented by warped product forms of Jacobi polynomials and their bases are patched to adjacent quadrilateral spectral elements.

$$\phi(x,y,z)=\tilde{\phi}_{lmn}x^{m+n}\Psi_m^{(0,0)}\left(\frac{y}{x}\right)\Psi_n^{(0,0)}\left(\frac{z}{x}\right)\Psi_1^{(2m+2n-1,0)}(x) \quad \text{in } \Omega^3. \tag{6}$$

The warped product representation leads to a separable product form for which efficient sum factorization techniques can be applied,

$$\phi(x,y,z)=\tilde{\phi}_{lmn}\Psi_m^{(0,0)}(u)\Psi_n^{(0,0)}(w)x^{m+n}\times\Psi_1^{(2m+2n-1,0)}(x) \quad \text{in } \Omega^3, \tag{7}$$

where $\Psi_{\underset{\sim}{m}}^{(p,q)}(x)$ are appropriately chosen Jacobi polynomials and $\tilde{\phi}_{lmn}$ are the expansion coefficients for the three-dimensional warp product representation. Similar approximations have been used in the context of general tetrahedral spectral elements proposed in [20] for solving the Helmholtz equation. The connection between Duffy's work and the warp product representation of [4] to effectively deal with r^{-1} singularities (up to r^{-p}; $p<3$ in three dimensions) has apparently gone unnoticed up to this point. The second and third methods are discussed below and both lead to numerical approximations that are similar in scaling of the condition number for the discrete system of Eq. (1) when compared to the traditional spectral element method [21].

For the warped product representation the application of boundary conditions requires recasting the basis into boundary conscious modes that contain surface modes and interior modes (which vanish at the pyramid boundaries). The surface modes include special expansions for the five corners, eight edges, and five faces. This allows for C^0 continuous boundary conditions to be applied across pyramid-pyramid boundaries. The optimal choice of Gaussian-type quadratures were GLL for the u and w components. For the x direction it was found that incorporation of the x weight and choice of an integration rule that did not include the vertex was the best method [22]; similar types of quadrature rules are described in [20] as well as the application of boundary continuous modes. The matching of a given pyramid base to a traditional spectral element face was done by the integral matching condition,

$$\int g_{mn}(s,t)[\phi_{ij}h_i(s)h_j(t)-\tilde{\phi}_{pq}g_{pq}(r,s)]dr\,ds, \tag{8}$$

where $g_{mn}(r,s)$ is the two-dimensional boundary conscious basis set associated with the base of the pyramid and $\tilde{\phi}_{mn}(r,s)$ are the expansion coefficients associated with the base modes of the three-dimensional boundary conscious expansion. This matching condition is not C^0 continuous at the interface but is minimizing in the L^2 norm and converges with the overall approximation scheme. The above minimizing statement leads to an algebraic system of equations that relates the collocation points of a GLL representation for a traditional spectral element formulation to the expansion modes of the warp product basis set,

$$\tilde{\phi}_{pq}=\mathbf{Z}\phi_{ij}\,. \tag{9}$$

This allows the pyramid-based system to be equated with adjacent quadrilaterals of the spectral element method by a standard direct stiffness summation.

The discrete Laplacian is formulated in a similar fashion as in [20] and only the relation of physical space gradients to those in the mapped space must be known. With application of the chain rule we arrive at Eqs. (10)–(12), where $\mathbf{x}=x$. The gradients in the mapped space $(\partial/\partial x,\partial/\partial u,\partial/\partial w)$ are formulated with the GLL interpolants in the (x,u,w) space as in the spectral element formulation.

$$\frac{\partial}{\partial \mathbf{x}}=\frac{\partial}{\partial x}-\frac{u}{\mathbf{x}}\frac{\partial}{\partial u}-\frac{w}{\mathbf{x}}\frac{\partial}{\partial w}, \tag{10}$$

$$\frac{\partial}{\partial y}=\frac{u}{\mathbf{x}}\frac{\partial}{\partial u}, \tag{11}$$

$$\frac{\partial}{\partial z}=\frac{w}{\mathbf{x}}\frac{\partial}{\partial w}. \tag{12}$$

We are then left with a representation of the discrete Laplacian as

$$\mathbf{A}\begin{bmatrix}\mathbf{Z}\phi_{ij}\\ \hat{\phi}_{lmn}\end{bmatrix},$$

where $\hat{\phi}_{lmn}$ are the expansion coefficients for the three-dimensional warp product basis set, not including the modes connected to the base of the pyramid and $\mathbf{A}$ is the discrete Laplacian formulated in the (x,u,w) space. With the addition of the pyramid to quadrilateral matching condition the algebraic system is no longer symmetric and a premultiplication with transpose of $\mathbf{Z}$ is performed giving the final system for the discrete Laplacian as

$$\begin{bmatrix}\mathbf{Z}^T & 0\\ 0 & \mathbf{I}\end{bmatrix}\mathbf{A}\begin{bmatrix}Z\phi_{ij}\\ \hat{\phi}_{lmn}\end{bmatrix}.$$

A similar representation is given for the diagonal singularity; Ref. [20] presents a more detailed treatment of variable coefficient Hemholtz equations.

The second approximation method for the numerical solution is a tensor product form of Lagrangian interpolants in the mapped space, $h_i(x)h_j(u)h_k(w)$. This formulation allows straightforward C^0 matching if the order of pyramid base quadrature is equal to that of the adjacent quadrilateral. In the above discussion for the warp product approximation the same discrete operator, $\mathbf{A}$ above, was formulated. The use of the C^0 matching and Lagrangian interpolants was found to give favorable overall computational efficiencies versus the warp product form. The discrete operators are formulated easily by the variational formulation and mapped space derivatives are calculated in the same fashion as the spectral element method, here the x component contribution of the Laplacian is given:

$$\begin{aligned}A^{x}_{lmn_{ijk}}\phi_{ijk}=&\int\int\int\frac{\partial}{\partial \mathbf{x}}[h_l(x)h_m(u)h_n(w)]\\ &\times\frac{\partial}{\partial \mathbf{x}}[h_i(x)h_j(u)h_k(w)]\\ &\times\phi_{ijk}x^2dx\,du\,dw\quad\text{in }\Omega^3.\end{aligned}$$

The integrand is a smooth function within the mapped cube of the pyramid domain and the remaining formulation and convergence estimates follow the traditional spectral element formulation for variable coefficient Helmholtz equations [21]. The warp product representation appears to add additional complexities to the formulation that are not apparently needed for three-dimensional variable coefficient Helmholtz equations. The following section presents results that validate both the warp product representation and the Lagrangian interpolants of the mapped space as effective formulations leading to exponentially converging numerical methods.

III. RESULTS

The resulting algebraic system was presented above and efficient numerical methods must be established for its inversion. Solutions of Eq. (1) are presented for $V(\mathbf{x})=0$ and various different asymptotic behaviors near the singularity. Exponential convergence rates are demonstrated for solutions with zero and nonzero values at the origin for the warp product representation in a cubic domain and discontinuous first derivatives, cusps, at the origin for an infinite domain. All solutions are obtained with precisely the same numerical procedure. Several different domain decompositions are presented, including pure pyramid as well as combined pyramid-quadrilateral decompositions. For cases in electronic structure theory where the additional potential, $V(\mathbf{x})$, does not vanish an extra term is added to the algebraic system; however, for a smooth potentials away from the singularity the exponential convergence is maintained by the method [8].

The first computational domain is a cube with edge di-

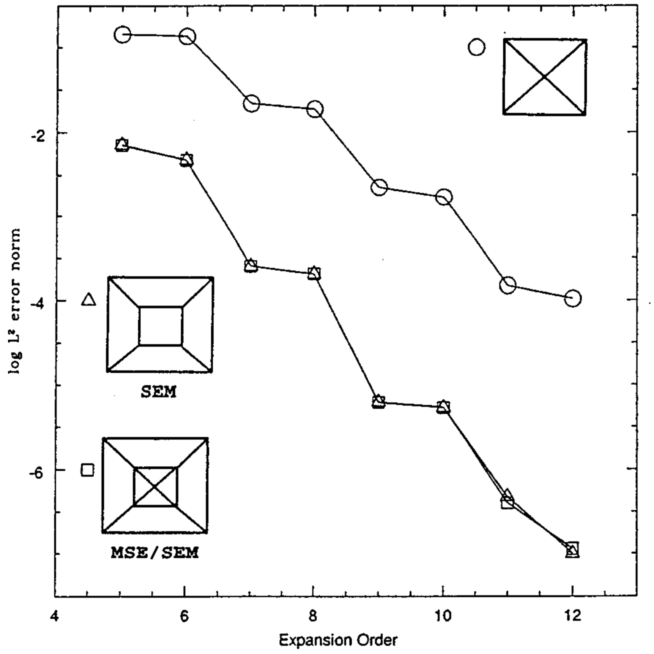

FIG. 2. The decay rate of the $\log_{10}$ of the L^2 error norm versus the number of quadrature points for the solution of the one electron operator is plotted here, where the solution is given by the function $u(\mathbf{x})=\sin(\pi x)\sin(\pi y)\sin(\pi z)$. The cubic domain was decomposed into six pyramids (○), seven quadrilaterals (△), and six pyramids matched to six quadrilaterals (□).

mension of 2 units, $[-1,1]$, and $Z=1$ in Eq. (1); for this domain the warped product form was used. The first solution studied was $u(\mathbf{x})=\sin(\pi x)\sin(\pi y)\sin(\pi z)$ with periodic boundary conditions applied in all three spatial directions; this solution is smooth and vanishes at the singularity. Both traditional spectral elements and molecular spectral elements can be used to solve this problem. Figure 2 plots the L^2 error norm for the solution via the SEM, MSE, and matched methods; the matched MSE-SEM solution used six pyramids and six quadrilateral where the pyramid height was taken to be 0.5. The SEM solution used seven quadrilaterals in a spider web decomposition of the cube; the interior cube had a half width of 0.5. The SEM and combined matched solutions perform equally as well in convergence. The solution with only six pyramids has roughly one-half the resolution and therefore has slightly larger errors; however, all three domain decompositions exhibit exponential decay with respect to the degree of the polynomial used in the approximation. For the pyramids the degree of the approximation is taken to be the highest degree polynomial used on the base. The next solutions are examined, which have nonzero values at the singularity. Two solutions are examined; the first having a continuous first derivative at the singularity, $u(\mathbf{x})=[1+\cos(\pi x)][1+\cos(\pi y)][1+\cos(\pi z)]$. The second solution exhibits an exponential decay at the singularity and is given by $u(\mathbf{x})=\exp[g(\mathbf{x})]-1$ where $g(\mathbf{x})=(1-x^2)(1-y^2)(1-z^2)$; here homogeneous Dirichlet boundary conditions were applied in all three spatial directions. Figure 3 plots the L^2 error norm for the later function with respect to the degree of the highest polynomial used. Results are presented for the six pyramid, six pyramid plus six quadrilaterals, and the six pyramid plus twelve quadrilaterals; the latter decomposition included a pyramid height of $\frac{1}{3}$. All solutions exhibited exponential convergence with respect to the polynomial degree. The cosine dependent solution studied gave similar results; the results for a spectral element method are not presented since it is known to be incapable of converging to the correct result. It should be noted that the six pyramid versus the pyramids plus 12 quadrilaterals have a five order of magnitude difference in their error norms for polynomials of degree eight and above. The added elements represented a factor of three in the spatial resolution that in principle should give only a factor of three decrease in error since the approximation error has only a linear dependence on element number; formally this demonstrates an h-p finite-element optimization. This sizable decrease in error is a demonstration of the power of spectral element methods once a suitable skeleton mesh is applied to a solution; in general once a spectral method has an adequate resolution the method converges rapidly with comparatively little extra work.

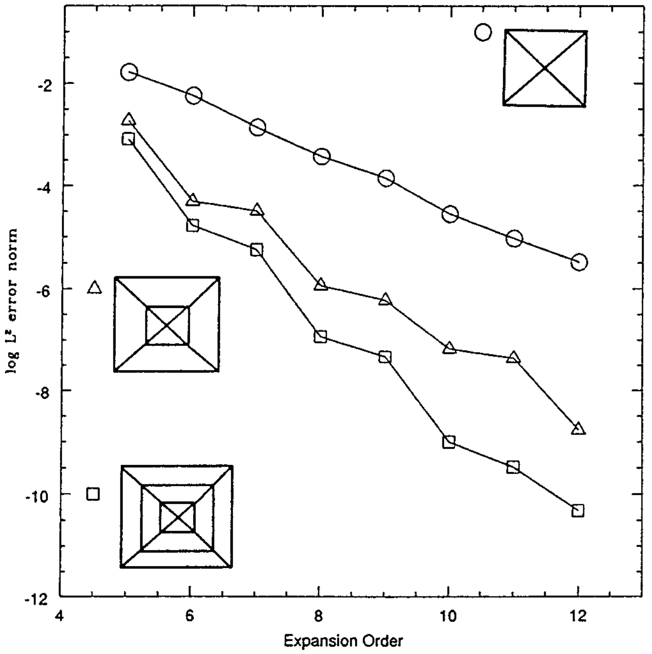

FIG. 3. The decay rate of the $\log_{10}$ of the L^2 error norm versus the number of quadrature points for the solution of the one-electron operator is plotted here, where the solution is given by the function $u(\mathbf{x})=\exp[g(\mathbf{x})]-1$; $g(\mathbf{x})=(1-x^2)(1-y^2)(1-z^2)$. The cubic domain was decomposed into six pyramids (○), six pyramids matched to six quadrilaterals (△), and six pyramids matched to 12 quadrilaterals (□). Exponential convergence is demonstrated with a nonzero solution value at the singularity location.

Next, the calculation of the hydrogenlike orbitals of nitrogen, $Z=7$ in Eq. (1), are presented as a demonstration of the ability to solve an eigenproblem with characteristics relevant to chemical physics. The exact solution can readily be obtained analytically and the eigenvalues are given by $\varepsilon_n=Z^2/2n^2$. The errors associated with the calculations of the first two eigenvalues versus increasing polynomial order are plotted in Fig. 4. The spectral element skeleton mesh and contour map of the $1s$ orbital are plotted in Fig. 5. The mesh consisted of a spider web structure close to the nuclei location with a cubic element that had a 0.08 a.u. edge length in which the pyramids were located. The domain radius was 9

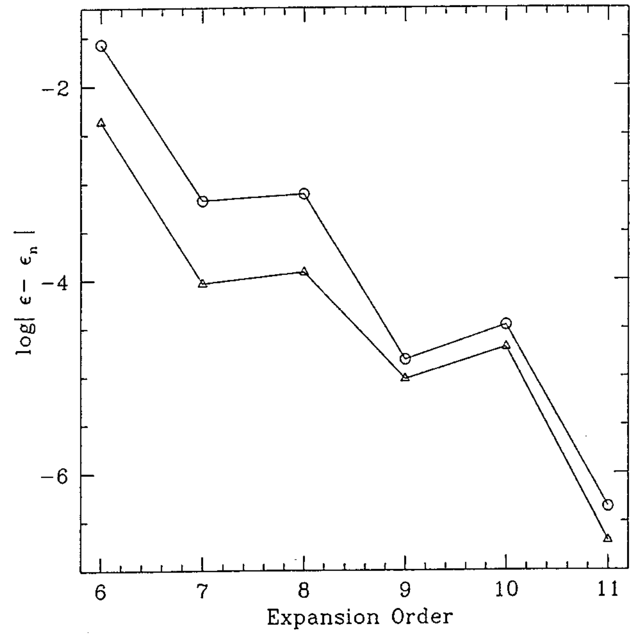

FIG. 4. The decay rate of the error in the orbital energy versus the number of quadrature points for the solution of the first two hydrogenlike orbitals of nitrogen is plotted here. The spherical domain was decomposed into 206 spectral elements with six pyramids around the nuclei and the domain radius for practical infinity was chosen as 9 a.u. Exponential convergence is demonstrated with a cusp present at the singularity location, where (○) indicates mode 1 and (△) indicates mode 2 convergence.

a.u. and this was taken as the practical infinity where the homogeneous Dirichlet boundary condition was applied. The mesh demonstrates the geometric flexibility of designing higher resolution in high gradient regions of the solution and lower resolution (larger elements) in the far field region; the domain consisted of 207 elements. Recent calculations of triatomic molecules using a very similar mesh have used 208 elements and the number of elements is not strongly influenced by slight increases in the number of nuclei.

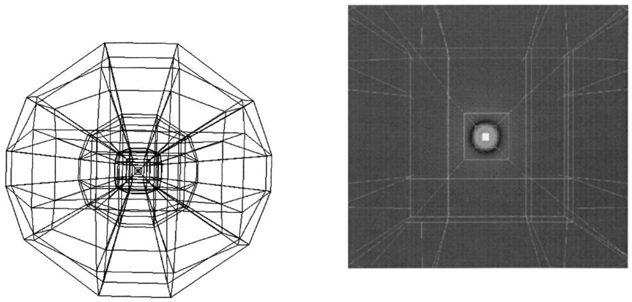

FIG. 5. The spectral element skeleton mesh used for the solution of the hydrogenlike orbitals of nitrogen is plotted here along with a contour map of the first orbital. The spherical domain was decomposed into 206 spectral elements with six pyramids around the nuclei and the domain radius for practical infinity was chosen as 9 a.u. The cubic subdomain at the center of mesh has an edge length of 0.08 a.u. and contains six pyramid spectral elements.

Inversion of the global algebraic system was carried out by a preconditioned conjugate gradient method. The preconditioning was accomplished with the diagonal of the discrete Laplacian. This choice of preconditioner was found to lead to scalings in the condition number of the overall system in agreement with the traditional spectral element method [3,21]. The number of conjugate gradient iterations were found to be larger for the warp product representation versus that of the Lagrangian interpolants; however, overall efficiency is maintained. Computational complexity of the matrix vector multiply scales as KN^4 for the pyramid as well as the quadrilateral decompositions; where K is the number of elements in the domain. Typically 100–700 preconditioned conjugate gradients were necessary, depending on the order of the polynomial, for the inversion of the Schrödinger-type operator. The eigenproblem was solved by an inverse subspace iteration method and fewer then ten iterations were necessary to converge the first two orbitals.

IV. SUMMARY

A numerical formulation has been presented and applied to the solution of the single-particle Schrödinger equation. The method exhibits exponential convergence rates in the degree of the polynomial used in the spectral approximation. The method can be universally applied to general multicenter systems in the context of electronic structure calculations. Solutions of operators with point singularities as high as r^{-p}, $p<3$, in three dimensions can be handled with spectral accuracy with this formulation. The method can be viewed as an extension of the spectral element method developed to solve elliptical partial differential equations. Issues of computational complexity scale in overall agreement with the traditional spectral element method. Successful numerical approximations of operators and integration of the point singularities were accomplished with the use of a Duffy transformation and suitable benchmark calculations were presented, including the hydrogenlike orbitals of nitrogen. Applications are currently being studied for large-scale molecular structures in the context of density functional theory, and the incorporation of an efficient eigensolver for the symmetric operator presented above is the subject of current research.

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