

Solution of the Hartree–Fock equations for polyatomic molecules by a pseudospectral method

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(Received 31 October 1986; accepted 2 December 1986)

A pseudospectral code for general polyatomic molecules has been developed using Gaussian basis functions. As an example, the water molecule is studied using a 6-31G** basis set. Quantitative agreement with conventional calculations is obtained for the equilibrium geometry, total energy, first ionization potential, and vibrational force constants. Timing results for a vectorized version of the code (run on a Cray X-MP) indicate that for large molecules, rate enhancements of Hartree–Fock self-consistent field calculations of order 10^3 can be achieved.

I. INTRODUCTION

For the past 30 years, the overwhelming majority of self-consistent field (SCF) electronic structure calculations have been carried out via the Roothaan basis set procedure.¹¹ This method has many attractive features; it is strictly variational, straightforward to implement numerically, provides clear prescriptions for optimization (e.g., of the basis set), and conforms well to chemical intuition. However, it is a highly inefficient method of solving a nonlinear, three-dimensional integro-differential equation. Indeed, analogous methods are rarely employed by engineers or applied mathematicians in large-scale computations of, e.g., fluid flow or mechanical stress. The consequence of this inefficiency has been to limit SCF calculations to a small basis set and (hence) to small, gas-phase molecules. Because of the rapid (N^4) growth of computational effort with basis set size, the next generation of supercomputers will only ameliorate (rather than remedy) this problem.

Various attempts have been made to develop numerical methods for solution of the Hartree–Fock equations.^{3–10} In general, these methods have suffered from one of two serious defects; either they are easily applicable only to atoms or diatomic molecules, or they have been incapable of achieving the high accuracy of conventional techniques. The source of this difficulty is twofold. First, the Coulomb singularities at the nuclei (which can be arranged in an arbitrarily irregular geometry) render traditional discrete methods (finite differences, finite elements, numerical quadrature) difficult and expensive. Second, the usual Rayleigh–Ritz variational scheme appears to have remarkable success in minimizing *relative* error. For example, the equilibrium geometry of the water molecule converges quite rapidly with basis set size (i.e., a 6-31G** basis gives an acceptably accurate H–O–H bond angle and O–H bond length) to the Hartree–Fock limit, despite the fact that the energy differences involved in locating this minimum are two orders of magnitude less than the absolute 6-31G** basis set error in the total energy. Numerical methods often have difficulty reproducing this property, which is essential if they are to be competitive for quantitative chemical applications on large molecules.

Of all the modern numerical techniques used for large-scale computations, the pseudospectral method of Orszag^{12–15} appears to have the greatest promise for studying chemical problems. In addition to the original applications to hydrodynamic simulations of isotropic turbulence and wall-bounded flows,^{16–20} variants of the method (not always recognized as such) have recently been applied to atom–surface scattering,^{21,22} vibrational bound state problems,²³ and motion of a quantum mechanical electron in a molten salt.²⁴

The key idea is the use of both a basis set (to improve accuracy in evaluating derivatives and integrals) and a physical space grid (on which to carry out multiplications), thus retaining the speed of discrete methods and the smoothing properties of continuous functions.

Modification of the ordinary pseudospectral approach allows a *synthesis* of traditional quantum chemistry methods with efficient numerical techniques. A global basis set of standard quantum chemical functions is employed, and emphasis is placed on recovering the Rayleigh–Ritz variational property by removal of aliasing errors (see Ref. 2 and below).

The numerical grid eliminates two-electron integrals and leads to an N^3 scaling of computation time and storage space, where N is the basis set size. Consequently, large rate enhancements in calculation of molecular wave functions are expected if sufficient accuracy can be achieved.

In two previous papers,^{1,2} it was shown that a numerical scheme based on the above principles yielded highly accurate total energies, equilibrium geometries, orbital energies, and force constants for atoms and diatomic molecules. While these results are encouraging, they provide no guarantee that application of the formalism in a fully three-dimensional system (where the basis set is necessarily less accurate) would be successful.

In this paper, we describe a general pseudospectral code for polyatomic molecules using Gaussian basis functions. The synthesis with conventional quantum chemistry has become more complete; two-electron integrals over four basis functions on the same atom are done explicitly (at negligible computational cost), and optimization of some nonlinear parameters is used to reduce error. The resulting algorithm can be thought of as a truly hybrid scheme, borrowing com-

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putational machinery and philosophy from both approaches.

The water molecule is studied as a simple test case. With a 6-31G** basis set, quantitative agreement with Raleigh-Ritz values for the total energy, first ionization potential, equilibrium geometry, and vibrational force constants are achieved. Strategies are described for optimization of the physical space grid and dealiasing functions. Timing results indicate that rate enhancements of $O(10^3)$ over conventional calculations can be expected for large basis sets.

II. ELECTRONIC STRUCTURE OF THE WATER MOLECULE AND ATOMIC BASIS SETS

We study the water molecule under the assumption of C_{2v} symmetry, i.e., the two O–H bond lengths are constrained to be equal. There are then three distinct symmetry groups: A_1 , B_1 , and B_2 , which we designate as groups 1, 2, and 3, respectively. Group 1 generates three occupied orbitals, while groups 2 and 3 produce one each. Group 2 has as a nodal surface the plane containing the molecule, while group 3's nodal surface is the plane bisecting the H–O–H bond angle.

The decomposition of the atomic basis sets into symmetry-adapted functions is straightforward and will not be described here in detail. We construct three disconnected blocks of the Fock operator and diagonalize each to obtain the new molecular orbitals in the iteration process.

We have chosen to utilize a 6-31G** basis set^{32,33} to study the water molecule. This basis set provides a crucial test of the pseudospectral method; it yields an equilibrium geometry in good agreement with Hartree–Fock limit calculations, but does not accurately reproduce the total energy. A basis set without polarization functions (e.g., 4-31G) would not possess the first property. There are thus 15 basis functions on the oxygen (3s, 6p, 6d) and 5 on each hydrogen (2s, 3p). When sorted into the appropriate symmetry groups, there are 12 functions in group 1, 4 in group 2, and 7 in group 3. Two functions do not transform as any of the above symmetry groups.

III. PSEUDOSPECTRAL METHOD FOR HARTREE–FOCK EQUATIONS

A. Basic formalism

The pseudospectral formulation of the Hartree–Fock equations used here is essentially that described in Refs. 1 and 2. The basic idea is to use both a physical space (i.e., grid) representation $\psi(r)$ and a spectral (basis set) representation \mathbf{c} of the occupied molecular orbitals, and transform between them. Producing function values on a grid given the basis set and coefficients is straightforward. The inverse transform is accomplished via a least squares procedure in which additional functions (dealiasing functions) are included and then discarded; this step is the only approximation (other than basis set incompleteness) made in the method. The number of grid points must be greater than or equal to the number of basis functions.

The use of dealiasing functions¹⁵ has proved to be crucial in obtaining accurate results with the pseudospectral

method. The pseudospectral Fock operator F_{ps} (see below) acts on a coefficient vector \mathbf{c} and produces a function on the physical space grid. This function can be well represented by the basis set, but there are some components produced (the alias) which are outside of the basis set. If left alone, these components are misinterpreted by the basis set, leading to fluctuations as a function of geometry which degrade the accuracy of the relative energy. By including additional functions, the great majority of the alias is filtered from $F_{ps}\mathbf{c}$, rendering the pseudospectral calculation nearly equivalent to a conventional one (in which the alias is exactly removed by analytic integration). More discussion of this can be found in Ref. 2.

The basis set coefficients satisfy the usual Fock equation

$$F\mathbf{c} = S\mathbf{c}E, \quad (1)$$

where S is the spectral overlap matrix, and F is given by

$$F = H_0 + 2J - K. \quad (2)$$

The operators H_0 (the standard one-electron Hamiltonian) and S are constructed by conventional analytic evaluation of integrals over the basis set. The two-electron operators J and K are formed via the equations

$$J = Q \cdot J_{ps}, \quad (3)$$

$$K = Q \cdot K_{ps}, \quad (4)$$

where J_{ps}, K_{ps} produce on the physical space grid the result of acting with the two-electron Coulomb and exchange operators on a coefficient vector \mathbf{c} . The operator F_{ps} is defined as $F_{ps} = 2J_{ps} - K_{ps}$.

Conventional electronic structure programs replace matrix multiplication by Q with analytic integration over the basis functions; this leads to a requirement to compute $\sim N^4$ two-electron multicenter integrals and to perform four index transforms in the SCF iteration procedure. Our discrete equations avoid both of these, saving substantial computation time but presenting problems in obtaining acceptable accuracy in relative energies. Note that the basis set error for the absolute energy is typically much larger than the difference between the conventional and pseudospectral results.

The operators J_{ps} and K_{ps} are constructed from the three-center one-electron integrals

$$A_{nm}(r_j) = \int \frac{\chi_n(r')\chi_m(r')}{|r_j - r'|} d^3r', \quad (5)$$

where χ_n, χ_m are the usual atomic basis functions. Formulas for J_{ps} and K_{ps} are given in Refs. 1 and 2.

The inverse operator Q is obtained from the normal least squares equations, which give the best fit of the basis and dealiasing functions to the result of the operation $F_{ps}\psi$, i.e.,

$$Q = [R^+ w R]^{-1} R^+ w. \quad (6)$$

Here, R is the matrix of basis and dealiasing functions on the grid, R^+ the transpose, and w a diagonal matrix of least squares weights. The dealiasing functions are initially orthogonalized to the basis set using analytic overlap integrals and hence are simply ignored in subsequent calculation. In the present program, the matrix Q is formed explicitly as in Eq. (6). For larger problems, this may be inefficient;

full matrix inversion can be avoided by solving linear equation systems directly in the eigenvector solver.

Once the Fock operator is constructed, the usual interaction of the pseudo-eigenvalue equations is used to obtain a solution. Canonical orthogonalization is employed to deal with the overlap matrix. Because the pseudospectral Fock operator is not necessarily Hermitian, a projection operator technique is used to enforce orbital orthogonality. We have improved the efficiency of the algorithm described in Ref. 2 by utilizing inverse iteration and by forming the projection operator more rapidly.

B. Atomic Fock operators

A straightforward modification of the above scheme is to partition the two-electron Fock operator into a sum of purely atomic terms, ΣF_a , and the remaining terms. We compute the F_a using conventional two-electron integrals (cf. Ref. 31). This is trivial computationally (e.g., the necessary integrals can be evaluated once and for all for any given basis set) and removes aliasing errors from the largest matrix elements. It also ensures that dissociation to the atomic limit yields the conventional Hartree-Fock result; note that all purely atomic terms are now computed spectrally.

In the present calculation on the water molecule, we apply this technique only to the oxygen atom because the symmetry considerations make it inconvenient to separate the hydrogen Fock operator into atomic parts. However, we have compared the pseudospectral and conventional atomic hydrogenic matrix elements, and the difference is quite small.

The above procedure does require assembly of the atomic Fock matrices F_a from the orbital eigenvectors and atomic two-electron integrals. A naive calculation would imply a computational effort proportional to N_a^4 , where N_a is the number of atomic basis functions. By exploiting symmetry, however, the number of nonzero atomic two-electron integrals is reduced considerably. Consequently, construction of the F_a constitutes a negligible fraction of the computation time per iteration.

IV. GRID AND DEALIASING DESIGN AND OPTIMIZATION

A. General considerations

In principle, the results obtained with pseudospectral code are nonlinear functions of the grid positions and the dealiasing parameters. In practice, it is not possible to optimize each of these separately starting from an arbitrary initial guess. Consequently, strategies must be developed for constructing grid and dealiasing parameters from a set of rules and a few variables which can be optimally adjusted. The methods described below represent an initial attack on this very complicated problem.

The strategies adopted in this paper have many *ad hoc* features; they were developed by a combination of physical reasoning, numerical experimentation, and the three optimization criteria discussed in Sec. IV D. Subsequent approaches may discard many of these features; they should not be regarded as demonstrably efficient in any comparative sense. The main purpose of this paper is to show that the

pseudospectral method can produce a quantitatively accurate solution for a polyatomic molecule. The robustness of the method will be addressed by displaying explicitly the results of parameter variation.

B. Grid architecture

Each atom "carries" a grid arranged in radial shells around the nucleus. Specification of an atomic grid then consists of assigning the following parameters: (1) number of radial shells; (2) position of each shell; (3) number of points per shell; and (4) angular dispersion of the points in each shell.

For the present problem, only one quadrant of a global coordinate system centered on the oxygen atom needs to be filled, because of symmetry. The oxygen grid contains either two or six points per radial shell, with angular coordinates given in Table I. Only one hydrogen atom is assigned a grid; each radial shell has either two or four points, whose angular positions are also given in Table I. Some of the points of the hydrogen grid will spill over into a different quadrant; this is inefficient, but causes no numerical problems.

Each radial grid is generated by specifying two regions, one for the core (short-range) basis and dealiasing functions, and one for the long-range valence functions. Each region has P radial shells. First, preliminary radial shells are defined by the inner and outer radius of each region and by the zeros of the Chebyshev polynomial of order $P + 1$; the actual points are embedded in the center of each preliminary shell. The Chebyshev spacing concentrates points nearer to the nucleus to resolve the exponential singularity there. Table II lists the positions and number of points for each oxygen and hydrogen shell. The parameters (inner and outer radii) used to generate this grid were: oxygen region I, 0.01–0.5; region II, 0.5–10.0; hydrogen region I, 0.01–0.2; region II, 0.2–10.0.

For the present calculation, we used 100 points for the oxygen grid and 68 for the hydrogen. This grid provides great stability; even large alterations in the inner and outer radii of the radial regions produce little change in many ob-

TABLE I. Angular dispersion of grid points in a radial shell of radius $R = 1$. x , y , and z are Cartesian coordinates relative to the nucleus.

Atom	Number of points	Point number	x	y	z
O	2	1	$1/\sqrt{3}$	$1/\sqrt{3}$	$-1/\sqrt{3}$
		2	$1/\sqrt{3}$	$1/\sqrt{3}$	$1/\sqrt{3}$
O	6	1	0.823	0.402	0.402
		2	0.402	0.823	0.402
		3	0.402	0.402	0.823
		4	0.823	0.402	-0.402
		5	0.402	0.823	-0.402
		6	0.402	0.402	-0.823
H	2	1	$1/\sqrt{2}$	$1/\sqrt{2}$	0
		2	$1/\sqrt{2}$	$-1/\sqrt{2}$	0
H	4	1	$1/\sqrt{3}$	$1/\sqrt{3}$	$1/\sqrt{3}$
		2	$1/\sqrt{3}$	$1/\sqrt{3}$	$-1/\sqrt{3}$
		3	$1/\sqrt{3}$	$-1/\sqrt{3}$	$1/\sqrt{3}$
		4	$1/\sqrt{3}$	$-1/\sqrt{3}$	$-1/\sqrt{3}$

TABLE II. Radial shell locations for the oxygen and hydrogen grids.

Shell No.	Oxygen grid		Hydrogen grid	
	Shell location ^a	Points/shell	Shell location ^a	Points/shell
1	0.027	2	0.016	2
2	0.076	2	0.035	2
3	0.153	2	0.066	4
4	0.255	2	0.105	4
5	0.373	2	0.150	4
6	0.5	6	0.2	4
7	0.552	6	0.271	4
8	0.708	6	0.484	4
9	0.964	6	0.836	4
10	0.32	6	1.32	4
11	1.77	6	1.93	4
12	2.31	6	2.66	4
13	2.94	6	3.50	4
14	3.64	6	4.43	4
15	4.41	6	5.44	4
16	5.25	6	6.52	4
17	6.13	6	7.65	4
18	7.06	6	8.81	4
19	8.02	6		
20	9.00	6		

^a Values are in a.u., and indicate distance from the radial shell to the corresponding nucleus.

servable properties. When better optimization techniques are developed, the number of grid points can undoubtedly be substantially reduced.

The least squares weight of each point is calculated from the volume of the radial shell in which it is embedded. Points which are enclosed in both the oxygen and hydrogen spherical grids have their weight divided by a factor of 2.

The actual weight of each point is the weight of the shell divided by the number of points per shell. A crude correction for the spillover of the hydrogenic grid onto the neighboring quadrant is made by dividing the weight of each point of the hydrogen grid by 2 if its distance from the hydrogen is greater than 1.8 a.u.

C. Dealiasing functions

Each atom is assigned a set of dealiasing functions. Conventional Gaussian functions are utilized in the present program. The problem is then to specify the exponents for the s , p , d , f , etc., functions to be employed.

The following approach is based on a combination of analytic arguments and empirical results of numerical experiments. As the ultimate goal is to develop a set of atomic parameters which are transferable to arbitrary polyatomics, the success of any derived rules will become apparent only when additional molecules have been studied. In fact, it is clear that better procedures will need to be developed; some ideas in this direction are presented in the conclusion.

Two considerations are important in choosing dealiasing functions. First, it is essential to use functions which project onto $F_{ps}c$. Second, the least squares collocation process should be as free from instability as possible. These two imperatives can come into conflict, although effective optimization of the grid would alleviate this problem.

The action of F_{ps} on c typically produces terms which have the form of a basis function multiplied by an integral

$A_{nm}(r)$ [cf. Eq. (5)]. The latter behaves like $1/r$ at long range; at short range, there are some fast components, but the dominant component is slowly varying. Higher angular terms are produced in accordance with the combination rules for spherical harmonics, e.g., the product of three d functions produces terms ranging from $l = 0$ to $l = 6$.

Because the valence and core functions have angular momentum of $l = 0$ or $l = 1$, a relatively small angular dealiasing set can be used. Here, we include functions up to f orbitals on the oxygen, and up to d orbitals on the hydrogen.

A second conclusion to be drawn from the above discussion is that the dealiasing exponents should be similar to those of the basis functions [perhaps somewhat larger, as the potential integrals $A_{nm}(r)$ do decrease away from the nucleus]. These considerations contribute to the empirical construction procedure for the dealiasing functions described below.

We begin by considering the valence (s and p for oxygen, s for hydrogen) dealiasing functions. A reasonable rule is to space the exponents by about a factor of 3. For oxygen, the initial (smallest) exponent is chosen to lie between the long-range (0.28) and medium-range (~ 1.0) exponents in the basis set, while for hydrogen, the initial exponent is similarly located between 0.12 and 0.44.

Problems can arise in terms of linear independence on the grid if the dealiasing set is too similar to the basis functions. For example, a gap (at $\lambda \approx 1.0$) in the hydrogen set was found empirically to improve results.

For the oxygen d functions, one exponent was set to 2.4 (three times the existing exponent of 0.8) while the other was set to 0.4 (slightly larger than the 0.28 s and p exponents it is intended to mimic). One f exponent of 6.0 (an intermediate value between the largest and smallest short-range s and p exponents) is included as well. Two hydrogen p exponents of 3.0 and 0.3 (bracketing the existing exponent of 1.1)

complete the initial dealiasing set. Decomposing the above functions into the three relevant symmetry groups for the water molecule (symmetry-adapted functions are used for the hydrogens) yields 27 functions for group 1, 11 for group 2, and 18 for group 3. The second of these totals is inadequate; this is a consequence of the expansion centers' location in the nodal plane of this group, ruling out, e.g., the use of linear combinations of hydrogen 1s functions. To remedy this deficiency, we include an additional d exponent on oxygen ($\lambda = 7.2$, or 3×2.4), an f exponent on oxygen ($\lambda = 0.4$), a d exponent on hydrogen ($\lambda = 3.0$), and p and d exponents between the two hydrogens ($\lambda = 3.0$). These additions contribute seven more symmetry-adapted functions, or 18 dealiasing functions in all for group 2.

In the next sections we describe several optimization criteria which are used (see the results section) to improve the above exponent values. However, the basic spacing principles are preserved; violation of this can cause difficulties.

D. Optimization criteria

Three general principles should guide the choice of grid locations and dealiasing functions. First, the dealiasing set should span the space of the alias produced by the pseudo-spectral Fock operator as closely as possible. Second, the basis set should possess as great a degree of linear independence as is possible on the grid. Third, the grid should be as close to an integration grid as is practical, i.e., one would like the condition

$$\sum_k \varphi_i(\mathbf{r}_k) \varphi_j(\mathbf{r}_k) \omega(\mathbf{r}_k) = \int \varphi_i \varphi_j d\tau \quad (7)$$

to be satisfied for all basis and dealiasing functions φ . However, note that the method is not dependent on Eq. (7) being accurately fulfilled for all functions; to achieve this, a much larger grid would have to be used.

Unfortunately, rigorous implementation of each of these conditions requires solution of extremely complicated nonlinear equations. Furthermore, the conditions are mutually interdependent; a change of dealiasing exponent may at the same time improve spanning of the alias and generate instability in the least squares collocation matrix. Thus, we concentrate below on the development of approximate, empirically based procedures.

Of the three general criteria, the last is the hardest to optimize beyond using least squares weights proportional to occupation volumes of the grid points. Hence this aspect of things is ignored here; it will certainly need to be considered further in subsequent work. A possible strategy is to use a nonlinear least squares routine to minimize the difference between the left- and right-hand sides of Eq. (7) by varying grid points.

Errors are amplified by the least squares procedure when the matrix $\mathbf{R}^+ \mathbf{w} \mathbf{R}$ (with diagonal elements normalized to unity) has small eigenvalues. The amplification has adverse consequences only to the extent that such eigenvectors

project onto the *basis* (as opposed to dealiasing) functions. To study this, we form the projection

$$P_\alpha = \left[\sum_{j=1}^{N_b} c_{j\alpha}^2 \right]^{1/2} / \epsilon_\alpha, \quad (8)$$

which represents the average error induced in the basis set by misinterpretation of an aliasing term by the eigenvector α with eigenvalue ϵ_α . The $c_{j\alpha}$ are the normalized eigenvector coefficients.

We must now translate this information into a procedure for evaluating the "goodness" of the parameter set: we choose here to study P_α for the smallest eigenvalue in each of the three symmetry groups, designating the resulting optimization parameters P_1 , P_2 , and P_3 . This approach will have to be modified when considering larger systems without symmetry, e.g., one might retain all eigenvalues below a cut-off threshold.

Two methods are used to examine the effectiveness of the dealiasing functions in removing the alias. The first is simple and direct; we calculate the difference between the spectral and pseudospectral *atomic* Fock operators F_a^{sp} and F_a^{ps} ; while the aliasing errors in F_a^{ps} are directly removed by replacement with F_a^{ps} (cf. Sec. II B), they provide a measure of the efficacy of the dealiasing procedure. Probably, errors should be weighted differently for polarization and valence matrix elements. Here, however, we simply sum the absolute value of all errors to arrive at a single number, the atomic aliasing error (AA) expressed in a.u.

The second criterion is to examine the Hermiticity of the Fock matrix. We exclude matrix elements between two polarization functions as being relatively unimportant. The mean square aliasing for each symmetry group σ is then defined as

$$\text{MSA} = \left[\sum_i \sum_j (F_{ij}^{(\sigma)} - F_{ji}^{(\sigma)})^2 / N_{el} \right]^{1/2}, \quad (9)$$

where N_{el} is the number of elements in the sum in Eq. (9). Hence, the MSA is the average error per matrix element.

Finally, the five optimization criteria must be employed in guiding development of the parameter set. A large value of AA reflects an inferior dealiasing set, and should be corrected (the question of what is "too large" must be studied empirically). Similarly, poor results are obtained if the MSA exceeds a certain magnitude. Small changes in either quantity are not very significant, as they represent very crude estimates of the efficacy of the parameter set (i.e., errors in some matrix elements may be much more relevant than in others).

On the other hand, P_1 , P_2 , and P_3 have proven to be sensitive indications of the accuracy in relative energies. Reduction of these quantities below empirically determined threshold values appears to be an effective way to ensure accurate calculation of the equilibrium geometry and force constants, as is demonstrated in what follows.

For the stability analysis carried out in Sec. V, the MSA varied minimally (this would not be true for more drastic variations of the grid and dealiasing parameters). Consequently, values of this quantity are not displayed in Tables V and VI. It was, however, used extensively in developing the empirical rules for dealiasing and grid design described above.

TABLE III. Dealiasing functions.

Function number	Location ^a	Type ^b	Exponent
1	O	1s	0.73
2	O	1s	2.2
3	O	1s	6.6
4	O	1s	17.9
5	O	1s	51.0
6	O	1s	150.0
7	O	2p	0.8
8	O	2p	2.5
9	O	2p	6.8
10	O	2p	18.0
11	O	3d ⁽¹⁾	0.4
12	O	3d ⁽²⁾	0.4
13	O	3d ⁽³⁾	0.38
14	O	3d	2.4
15	O	3d ⁽²⁾	7.2
16	O	4f ⁽¹⁾	10.0
17	O	4f ⁽²⁾	6.0
18	O	4f ⁽³⁾	6.0
19	O	4f ⁽²⁾	0.4
20	H	1s	0.3
21	H	1s	2.8
22	H	1s	9
23	H	1s	27
24	H	2p	0.3
25	H	2p	3
26	H	3d ⁽²⁾	3
27	B	2p ⁽²⁾	3
28	B	3d ⁽²⁾	3

^aO = oxygen, H = hydrogen (symmetry adapted linear combinations are employed), B = between the two hydrogen atoms.

^bSuperscripts indicate that only functions belonging to the designated symmetry group are included. The absence of a superscript implies that all angular functions consistent with the angular quantum number (*s*, *p*, *d*, or *f*) are classified into the appropriate symmetry groups and utilized.

V. RESULTS

A. Accuracy of the potential surface

Twenty-five water geometries ($R = 1.76$ – 1.80 in steps of 0.1 , $\theta = 101.4^\circ$ – 108.6° in steps of 1.8°) were employed in each generation of a potential surface. A quadratic least squares fit was then made to extract the equilibrium position (R_e, θ_e) and the force constants f_{RR} , $f_{R\theta}$, and $f_{\theta\theta}$. The latter are expressed in atomic units, with the angles measured in

radians. The above procedure for computing force constants is not highly accurate, but should be adequate for present purposes, which are the establishment of agreement in the 5%–10% range.

Note that in the above paragraph, θ refers to the H–O–H bond angle while R designates the O–H bond length of both O–H bonds. The least squares fit for the coefficient of the quadratic term in R is actually the sum of the symmetric and antisymmetric force constants. Consequently, we utilize the value of the antisymmetric force constant of -0.005 from Ref. 26 to obtain f_{RR} from the fitted coefficient.

Energies were converged to 10^{-8} a.u. Convergence of the Hartree-Fock iteration procedure was unproblematic, starting from a rather poor initial guess. No attempts were made to optimize this aspect of the program.

Using the optimization criteria, general principles, and initial exponents described in Sec. IV, a relatively small number of unsystematic parameter variations produced the results shown in Table IV. The precise grid configuration and set of dealiasing functions are listed in Tables I–III.

The equilibrium geometry is reproduced quite accurately, while force constants differ from Hartree-Fock limit values by roughly 5% or less (see Table IV). This performance is quite comparable to that of a conventional calculation using a 6-31G** basis set. Thus, assuming the procedures here can be systematized, refined, and efficiently applied to general polyatomics, the pseudospectral method is capable of matching a spectral program in converging relative energies long before the total energy is at the Hartree-Fock limit.

The total energy obtained here by the pseudospectral code is somewhat lower (0.004 a.u.) than the spectral 6-31G** result. To some extent, this is due to a decision to optimize relative as opposed to absolute aliasing error. This has no serious practical consequences as the discrepancy is an order of magnitude less than that for either calculation as compared to the Hartree-Fock limit. Nevertheless, refinement of the grid (which has a strong effect on the MSA criterion, the best predictor of total energy) could reduce this discrepancy.

We now turn to a discussion of numerical stability and efficacy of the optimization criteria. First, several global considerations will be briefly discussed without displaying detailed calculations. The grid used here is one of many

TABLE IV. Comparison of pseudospectral and conventional calculations on the water molecule.

Property	Conventional		Near Hartree-Fock limit ^c	
	4-31G ^a	6-31G** ^b	Fock limit ^c	Pseudospectral
Total energy	-75.907	-76.023	-76.065	-76.027
R_e	1.797	1.782	1.776	1.782
θ_e	112	106.0	106.1	105.0
f_{RR}	0.632	0.603
$f_{\theta\theta}$	0.179	0.182
$f_{R\theta}$	0.030	0.032
First ionization potential	0.500	0.497	0.506	0.497

^aReference 25.

^bReference 25.

^cReference 26.

TABLE V. Effect of 10% variation of dealiasing exponents.

Case	Perturbed function ^a	R_e	θ_e	f_{RR}	$f_{\theta\theta}$	$f_{R\theta}$	P_1	P_2	P_3	ΔAA
0	none	1.782	105.0	0.603	0.182	0.0318	4.48	1.24	1.04	0
1	1	1.782	105.0	0.609	0.182	0.0325	4.32	1.24	1.04	0
2	2	1.782	105.0	0.603	0.182	0.0318	3.66	1.24	1.04	0
3	3	1.783	104.9	0.603	0.182	0.0328	3.97	1.24	1.04	0
4	4	1.781	105.0	0.599	0.183	0.0305	4.67	1.24	1.04	0
5	5	1.782	105.0	0.602	0.182	0.0317	4.67	1.24	1.04	0
6	6	1.782	105.0	0.603	0.182	0.0318	4.48	1.24	1.04	0
7	7	1.786	104.7	0.569	0.172	0.0315	5.32	1.96	0.83	0.03
8	8	1.781	104.9	0.612	0.187	0.0313	3.58	0.75	1.07	0.01
9	9	1.787	105.0	0.583	0.172	0.0367	7.01	0.66	1.15	0
10	10	1.783	105.4	0.612	0.187	0.0377	6.63	1.24	0.62	-0.01
11	11	1.782	105.0	0.600	0.181	0.0306	8.65	1.24	1.04	-0.01
12	12	1.783	104.7	0.606	0.183	0.0315	4.48	0.617	1.04	0
13	13	1.783	104.1	0.603	0.184	0.0346	4.48	1.24	0.90	0
14	14	1.783	105.4	0.594	0.180	0.0351	3.76	1.10	1.03	0.07
15	15	1.783	104.8	0.594	0.180	0.0327	4.48	1.21	1.04	0.015
16	16	1.780	104.4	0.590	0.186	0.0254	7.01	1.24	1.04	0
17	17	1.782	104.6	0.592	0.184	0.0301	4.48	1.08	1.04	0
18	18	1.781	105.0	0.600	0.191	0.0319	4.48	1.24	1.01	0
19	19	1.782	105.4	0.594	0.178	0.0332	4.48	2.90	1.04	0

^aThe exponent of the corresponding function in Table III was increased 10%, with all other exponents held constant.

which yields reasonable results. Poor grids are signalled by large MSA values, with those from symmetry group 2 exhibiting the greatest sensitivity. Further discussion of grid optimization will be deferred to a subsequent paper in which superior construction algorithms will also be developed.

We next consider the effect of varying dealiasing exponents. To keep the data manageable, only oxygen exponents are varied; similar results are obtained for the remaining functions. Table V displays the results obtained on increasing each exponent by 10%, holding the remainder constant. For both Tables V and VI, ΔAA is the AA of the relevant case minus AA for the reference case (case 0 in Table V).

Several points are immediately apparent upon a cursory examination. First, the equilibrium geometry exhibits very small fluctuations, as do f_{rr} and $f_{\theta\theta}$. On a percentage basis, $f_{r\theta}$ deviates from the HF limit results of Table IV by as much as 30%. This can be partially attributed to its small absolute magnitude and/or inaccuracies in the least squares fitting routine.

Second, a few simple rules concerning the optimization criteria suffice to eliminate almost all of the more inaccurate

results. Case 14 suffers from poor agreement with atomic spectral integrals, while cases 7, 9, 10, 15, and 19 have at least one projection P_j which increases by 50% or more over the starting parameter set. The only unclear case is 13, which would be predicted to be at roughly the same accuracy level but suffers a degradation of θ_e and $f_{r\theta}$. This indicates that further development of optimization criteria will be required. The remaining parameter sets all exhibit comparable accuracy to the original one.

As the s and p dealiasing functions are constrained to approximately multiples of 3 ratios on physical grounds, it is inappropriate to study substantial variations of them. In Table VI, the remaining exponents are increased 50% to study the effect of a rather large perturbation. Cases 4, 7, 8, and 9 display $\approx 100\%$ increases in a projection P_j ; case 4 also suffers from an extremely large increase in the atomic aliasing error. Again, variation of the long-range d function for group 3 (case 3) yields inferior results which are not predicted by the optimization criteria.

In summary, we believe that the results shown here are quite encouraging with regard to the possibility of designing

TABLE VI. Effect of 50% variation of dealiasing exponents.

Case	Perturbed function ^a	R_e	θ_e	f_{RR}	$f_{\theta\theta}$	$f_{R\theta}$	P_1	P_2	P_3	ΔAA	Total energy
1	11	1.782	105.0	0.589	0.180	0.0294	7.40	1.24	1.04	-0.06	-76.027
2	12	1.785	104.5	0.604	0.183	0.0319	4.48	1.04	0.78	0.01	-76.028
3	13	1.785	103.6	0.612	0.188	0.0370	4.48	1.24	0.93	-0.02	-76.028
4	14	1.781	106.7	0.543	0.186	0.0237	8.48	0.40	0.56	0.25	-76.022
5	15	1.783	104.7	0.590	0.176	0.0325	4.48	1.4	1.04	-0.02	-76.028
6	16	1.786	104.9	0.592	0.177	0.0333	12.0	1.24	1.04	0	-76.027
7	17	1.783	104.3	0.548	0.186	0.0212	4.48	8.0	1.04	0	-76.026
8	18	1.776	104.9	0.617	0.216	0.0301	4.48	1.24	2.84	-0.02	-76.030
9	19	1.783	107.2	0.567	0.146	0.0332	4.48	2.76	1.04	0.015	-76.021

^aThe exponent of the corresponding function in Table III was increased 50%, with all other exponents held constant.

a general, accurate polyatomic pseudospectral program. This is particularly true in view of the level of effort needed to produce the above calculations; the length and complexity of the computer code is considerably reduced from that of a conventional *ab initio* program.

B. Timing results

All computations were performed on the University of Texas Center for High Performance Computing Cray X-MP supercomputer. Extensive use has been made of CRAY assembly language software, as described below. However, the routines utilized are for standard operations (matrix multiply, vectorized conditional statements), so that analogous packages exist on other systems (e.g., Cyber 205).

We concentrate on the computational steps which scale like N^3 , i.e., potential integral generation [cf. Eq. (5)] and Fock matrix assembly. For the present calculation, these steps actually consume a negligible fraction of computation time; they will, however, dominate for large molecules.

The formulas of Ref. 31 were used in constructing all Gaussian integrals. Most of the required operations are easily vectorized over the grid points. However, some care is required in evaluating the primitive functions $F_\nu(t)$. Efficient algorithms exist for $t < 1$ and $t > 1$. Unfortunately, the vector of t values for each three-center integral is not ordered, and will typically vary wildly in magnitude for each integral. A direct sorting algorithm would be very inefficient.

The solution adopted here is tabular interpolation combined with a change of variable. Defining $x = 1/(1+t)$, we construct a table of 10 000 values of each $F_\nu[t(x)]$, with x ranging from 0 to 1 in equally spaced intervals. For $t > 1$, the function $F_\nu(t) \times t^{\nu+1/2}$ is stored, while for $t < 1$, the table contains $F_\nu(t) \times 1.0$. It is important to include the value $t = 1$ (for which $t^{\nu+1/2} = 1$) explicitly in the table.

In evaluating $F_\nu(t)$ for arbitrary t , the first step is to use the vector conditional CVMGP hardware routine to set a variable SCALE equal to either 1.0 or $t^{\nu+1/2}$. The value of x is then computed from t , and linear interpolation on the table is multiplied by SCALE to produce the final result. The entire procedure is performed in one vectorized loop and requires about ten operations per value of t .

The advantage of this approach is easily understood by examining $F_0(t) \propto 1/t^{1/2} \text{erf}(t^{1/2})$. [Note that $F_\nu(t) \propto (1/t^{\nu+1/2}) \text{erf}(t^{1/2})$ as $t \rightarrow \infty$ for all ν .] $F_0(t)$ itself is slowly varying on the interval $[0,1]$; however, it is impractical to directly construct an interpolating table which accurately evaluates larger arguments (t can easily reach a value of 10^5). On the other hand, $\text{erf}(t^{1/2})$ rapidly approaches its asymptotic value of 1 for $t > 1$, so that this function can utilize widely spaced interpolating points in this region. The scaling function $1/(1+t)$ provides appropriate point spacings, i.e., large spacing for $t \gg 1$, small for $t \leq 1$. An accuracy level of 10^{-8} for all integrals was achieved with a 10 000 point table for each $F_\nu(t)$.

To facilitate comparisons with conventional methods, the two-electron integrals for H_2O in a 6-31G** basis *excluding d functions* were computed by the *ab initio* program TEXAS (written by Pulay).⁴⁰ *d functions* were excluded be-

cause, unlike our pseudospectral code, the version of TEXAS used here does not utilize genuine Cartesian d functions. The resulting basis set contains 36 primitive Gaussians. To allow calculation of computation time per primitive integral, the integral cutoff was set to zero. Total integral evaluation time was 1.37 s, leading to an average rate of $(36)^4 / (8 \times 1.37) = 162\,000$ integrals per second.

We used the same 36 Gaussian functions and a grid of 120 points; this required 0.020 s of computation time. The net rate of integral generation is thus $[(36)^2 \times 120] / (2 \times 0.02) = 3\,900\,000$ integrals/s. This implies a ratio of about 24:1 in individual primitive integral computation time.

The integral package of TEXAS has not been vectorized. However, vectorization of conventional *ab initio* integral routines is very difficult; a typical result is achievement of a factor of 2 improvement.³⁰ On the other hand, our program does not combine the $2s$ and $2p$ shells and is not fully optimized with regard to minimizing the number of actual operations [for example, a special routine could be written to evaluate $F_\nu(t)$ when it is known that all t will be $\gg 1$]. Thus, the above timing ratio appears reasonable when projecting improvement of both approaches.

To proceed further in timing comparisons, we must estimate the number of grid points required per basis function. Taking the largest symmetry block of 12 functions, we arrive at a figure of roughly 15 grid points per function. While this can almost certainly be reduced substantially by optimization, a fully three-dimensional grid (as opposed to confinement to one-quarter of the volume) will probably require a compensating increase, thus motivating use of the present value. Integral cutoffs will affect the performance of both programs considerably; we defer examination of this to a later paper, and here assume that equivalent reductions can be obtained.

Designating N as the number of basis functions and N_p as the number of primitives, we estimate $N_p \approx 2N$ for typical contraction schemes. We then obtain the scaling

$$t_{\text{int}}^{(\text{ps})} \sim (2N)^2 \cdot 15N/2 \quad (10)$$

for the pseudospectral approach and

$$t_{\text{int}}^{(s)} \sim (2N)^4/8 \quad (11)$$

for a conventional algorithm. Using the above ratio for primitive integral calculation yields

$$t_{\text{int}}^{(s)}/t_{\text{int}}^{(\text{ps})} = 24N/15 = 1.6N. \quad (12)$$

This leads to a factor (for a double zeta plus polarization basis) of $O(10)$ for a small molecule, $O(100)$ for a medium-sized molecule, and $O(1000)$ for a large molecule. Large basis set calculations should become inexpensive for the first time; integral generation for 400 basis functions would require only 320 CPU s, not considering the effects of integral cutoffs (which should drastically reduce this value).

We next discuss Fock matrix assembly. All of the requisite operations can be programmed as calls to the Cray assembly language matrix routines like MXMA and MXVA. This results in a factor of 5–10 enhancement beyond vectorization. For the present problem, Fock assembly time per iteration was less than 10^{-3} CPU s (as compared to 10^{-1} s

for TEXAS). This comparison is not really rigorous because symmetry block factorization was not employed in TEXAS. However, it seems clear that substantial gains will be realized in this part of the calculation. Furthermore, initial calculations can be run using a reduced grid (perhaps by a factor of 5), so that only a few expensive iterations need be performed. The latter statement also implies that integrals for this last stage can be profitably recalculated at each iteration, reducing storage space requirements.

VI. CONCLUSION

Two important points have been demonstrated in this paper. First, our version of the pseudospectral method is capable of producing quantitatively accurate results for a polyatomic molecule using a basis set of moderate quality. Second, substantial computation time reductions can be achieved in both integral evaluation and Fock matrix assembly. The magnitude of improvement in computational efficiency is sufficiently great that one can easily imagine doing accurate HF calculations on molecules which have previously been considered too large to treat at any level other than a minimal basis set one. It is this prospect which justifies the large investment in software development which will be required to transform the method from a research problem into a working tool of the quantum chemist.

The next logical step is to treat fully three-dimensional systems (with no symmetry) and to systematically study a series of small molecules using various basis sets. During this time, we will focus on optimization of the grid and dealiasing functions. Some promising possibilities include: (1) use of adaptive grids³⁹; (2) further exploration of bond-type dealiasing functions, also use of angular functions with $l > 3$; and (3) increase in the number of dealiasing functions, coupled with direct removal of functions which produce small eigenvalues of the least squares collocation matrix.

The present results do not by any means establish the pseudospectral approach as a definitive replacement for conventional Hartree-Fock programs; this can only be asserted if a single, automated program can produce accurate answers for an arbitrary molecule, with order of magnitude reductions in computation time. They do suggest that this goal is a realistic one. A contrast in this regard can be made with other numerical approaches, which typically have had difficulty in establishing either time advantages or adequate accuracy or both, even for diatomics.

The importance of the details of numerical implementation should be stressed; the quality of results achieved is quite sensitive to these details. For example, a recent paper by Thole²⁹ derives (independently) and employs basic equations which are similar to those of Refs. 1 and 2. However, total energies for the CO molecule displayed errors of ≈ 0.05 a.u. in the total energy despite the use of 575 grid points (our diatomic calculation on Li_2 used only 28 grid points and obtained agreement to 10^{-4} a.u. for the total energy). Computation times were comparable to or greater than in conventional calculations. The large errors are possibly attributable to failure to utilize dealiasing functions, although other numerical subtleties (e.g., how orbital orthogonality is enforced) may play some role.

At this point in the pseudospectral method's development, some comparisons with the numerical methods used to solve the SCF equations of local density functional (LDF) theory can be attempted. A variety of approaches which can in principle yield accurate results (within the context of the LDF approximation) have been developed.^{27,28,34-38} We choose to examine the discrete variable method (DVM) of Ellis and co-workers,^{35,36} which is similar in many respects to the approach taken here.

Both algorithms utilize a grid and a basis set (the DVM actually has auxiliary basis sets as well). The action of the SCF Hamiltonian on an orbital vector is eventually computed on the grid. To return to the basis set, the DVM employs direct numerical quadrature. Our operator Q [cf. Eq. (6)] would in fact be equivalent to the DVM formulation if the matrix $\mathbf{R}^+ \mathbf{wR}$ was the identity matrix. This will be true in the limit that the grid reproduces analytic overlap integrals accurately.

Our experience has been that this requires a very large number of grid points. Indeed, Ref. 35 indicates that convergence of the SCF solutions to the accuracy obtained here (it is, unfortunately, difficult to make precise comparisons in this regard) requires at least several thousand grid points per atom. The use of Eq. (6) combined with dealiasing appears to yield a substantial reduction in computational effort by allowing a much sparser mesh to be utilized. Thus, this aspect of the algorithm suggested here could be profitably applied to LDF calculations.

A second difference is the use of charge density fitting in the DVM. This procedure is probably uneconomical for the HF equations because many product densities of the form $\varphi_j \chi_k$ (where φ_j is a molecular SCF orbital and χ_k is a basis function) would have to be expanded in order to construct the nonlocal HF exchange operator. For the LDF equations, the obvious advantage of this approach is the reduction of integral storage. Given that this is not an issue, comparison of computation times is not straightforward, and would have to be made explicitly.

One point emphasized in Ref. 35 is the use of comparable approximations in various parts of SCF calculations. This philosophy is also advocated here; the great numerical precision of conventional HF calculations is meaningless in view of the basis set and correlation errors. As long as relative energies are evaluated with an accuracy in line with the errors inherent in the approximations, the failure to satisfy the Rayleigh-Ritz variational criterion exactly is irrelevant.

Prospects for proceeding beyond gas phase Hartree-Fock calculations also appear promising. Some of the important possibilities are (1) solution of MCSCF equations (where the high velocity of Fock matrix assembly should be very important), (2) incorporation of an external environment or pseudopotentials by direct evaluation of the effective field on the physical space grid, (3) application to solid state problems, and (4) density functional theory, possibly using an effective nonlocal exchange-correlation potential.

ACKNOWLEDGMENTS

This research was supported in part by grants from the National Science Foundation and the Robert A. Welch

Foundation. We thank Dr. Laurette Tuckerman for many invaluable discussions and assistance in code development, and Dr. J. E. Boggs for supplying results from the *ab initio* program TEXAS.

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