

# Pseudospectral Hartree–Fock gradient calculations

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Techniques for the calculation of analytic first derivatives of the Hartree–Fock energy are reported, within the context of the pseudospectral *ab initio* method. Using these gradients, geometry optimization is carried out on several molecules at the 6-31 G\*\* level. The resultant geometries are compared to those from conventional *ab initio* molecular-orbital calculations, and it is shown that bond lengths agree to within 0.003 Å, while bond angles are within 1°.

## I. INTRODUCTION

In a series of previous papers,<sup>1–7</sup> we have described a novel method for solving the self-consistent equations of electronic structure theory. The method is a hybrid of conventional quantum chemical procedures (e.g., local Gaussian basis sets) with the pseudospectral (PS) method,<sup>8</sup> a numerical procedure which utilizes both a physical space grid and a basis-set representation of the molecular orbitals. Agreement with conventional Roothaan–Hall<sup>9</sup> (RH) codes to 0.1 kcal/mol for the total energy has been demonstrated<sup>6,7</sup> for both Hartree–Fock (HF) and generalized valence bond<sup>10</sup> (GVB) calculations for a large set of molecules composed of first-row atoms. Furthermore, improvements of an order of magnitude in CPU time have been achieved<sup>7</sup> on a 20-atom HF test case (glutamine) as compared to any RH code using a direct version of the PS method in which full integral recalculation is employed. For molecules of this size, the PSHF method scales in practice as  $N^2$  (reduced from a formal  $N^3$  dependence by the use of cutoffs on local functions), to be contrasted with the  $N^3$  scaling (reduced from a formal  $N^4$ ) of GAUSSIAN 88.

These highly successful tests indicate that the PS method is likely to be the method of choice for self-consistent *ab initio* computations on large molecules. However, it is necessary to establish that the method performs adequately for calculations other than those for the total energy. In particular, accurate evaluation of analytic derivatives is essential if the method is to be of practical utility. The achievement of sufficiently high accuracy is nontrivial because of the use of the numerical grid, which is quite capable of introducing spurious variations in the total energy as a function of geometry due to alterations of the numerical integration scheme as atoms (and hence the atom-centered grids) are moved.

Analytic derivative methods for numerical self-consistent electronic structure calculations have been presented by others,<sup>11</sup> almost exclusively in the context of local-density-functional theory. However, these results have generally encompassed relatively small molecules, which are much less demanding in terms of the numerical precision required to

obtain converged results. There have been few (if any) systematic studies of large, complicated molecules in which it has been unambiguously shown that the local-density limiting geometry has actually been obtained to a specified level of accuracy. Such demonstrations are necessary if one wishes to establish the expected reliability (whatever electronic structure model is to be used) in a determination of relative conformational energies and structures in complex systems, an increasingly important task in biological modeling and materials science applications.

The present paper is concerned with establishing such behavior for the PS method in the context of HF theory (preliminary results indicate analogous accuracy is achieved for GVB computations as well). Our objective is to reproduce the RH geometry with the same basis set as closely as possible, thereby validating the PS procedure as an isomorphic replacement for RH. The accuracy of the PS procedure is then determined strictly by the basis set and level of electron correlation, and the huge literature on the reliability of *ab initio* RH geometries can be taken over.

Future papers will present detailed timing comparisons of PS and RH methods of geometry optimization. Substantial gains can be made not only in the cost of an individual step, but in the sequence of steps used to converge to the correct geometry. At present, however, we do not have a serious geometry optimization program in place. We will therefore restrict our discussion of efficiency to the comments that (a) generation of the PS gradient is considerably less expensive than the self-consistent-field (SCF) convergence procedure; and (b) obtaining an accurate gradient is easier than obtaining accurate total energies, due to the smoothing of error achieved by analytic differentiation. These two observations suggest that the PS method can yield significantly greater increases in efficiency for geometry optimization than for single-point energy calculations. A rigorous documentation of this point will be a subject of future communications.

The present paper focuses on demonstrating the accuracy of the PS method as compared to RH results with the same basis set. Both methods are allowed to converge to their own equilibrium geometries, and these geometries are then compared. In Sec. II our formulation of the PS gradient procedure is presented. Section III displays results for a series of small molecules and for glycine, a relatively complicated test case. All of these tests yield highly satisfactory results, in that the discrepancies between the PS and RH

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geometries are uniformly much smaller than those obtained in comparisons with experiment. Section IV briefly discusses future directions.

## II. METHOD

### A. Basic theory

The Hartree–Fock energy can be written as

$$E_{\text{HF}} = V_{\text{nuc}} + 2 \sum_{ij} P_{ij} H_{ij}^0 + \sum_{ijkl} P_{ij} P_{kl} [2(ij|kl) - (ik|jl)], \quad (1)$$

where  $V_{\text{nuc}}$  represents the nuclear–nuclear repulsion, the one-electron Hamiltonian  $H^0$  contains kinetic and potential terms, and the density matrix  $\mathbf{P}$  is the following combination of molecular-orbital coefficients:

$$P_{ij} = \sum_{\alpha} c_{i\alpha} c_{j\alpha}. \quad (2)$$

The two-electron integrals in (1) are defined by

$$(ij|kl) = \int \int \phi_i(1) \phi_j(1) \frac{1}{r_{12}} \phi_k(2) \phi_l(2) d\mathbf{r}_1 d\mathbf{r}_2, \quad (3)$$

where the  $\phi_i$  are basis functions. Note that  $(ij|kl)$  is symmetric with respect to interchange of indices  $i$  and  $j$ ,  $k$  and  $l$ , or  $ij$  and  $kl$ .

If  $X_A$  is one of the three coordinates ( $x$ ,  $y$ , or  $z$ ) of nucleus  $A$ , it can be shown<sup>12,13</sup> that the first derivative of (1) with respect to  $X_A$  has the form

$$\begin{aligned} \frac{\delta E_{\text{HF}}}{\delta X_A} = & \frac{\delta V_{\text{nuc}}}{\delta X_A} + 2 \sum_{ij} P_{ij} \frac{\delta H_{ij}^0}{\delta X_A} - 2 \sum_{ij} W_{ij} \frac{\delta S_{ij}}{\delta X_A} \\ & + \sum_{ijkl} P_{ij} P_{kl} \frac{\delta [2(ij|kl) - (ik|jl)]}{\delta X_A}, \end{aligned} \quad (4)$$

where  $\mathbf{S}$  is the usual overlap matrix, and  $\mathbf{W}$  is the energy-weighted density matrix

$$W_{ij} = \sum_{\alpha} \epsilon_{\alpha} c_{i\alpha} c_{j\alpha}. \quad (5)$$

The  $\epsilon$  appearing in (5) is the orbital energy from the Hartree–Fock equation

$$\mathbf{F}c_{\alpha} = \mathbf{S}c_{\alpha}\epsilon_{\alpha}. \quad (6)$$

Note that this formulation of the gradient avoids explicit differentiation of the density matrix  $\mathbf{P}$ .

### B. Pseudospectral approach

The first three terms on the right-hand side of (4) are not difficult computationally, and we evaluate them by standard methods<sup>13,14</sup> in spectral (atomic orbital) space. The final term,

$$\sum_{ijkl} P_{ij} P_{kl} \frac{\delta [2(ij|kl) - (ik|jl)]}{\delta X_A}, \quad (7)$$

involves derivatives of two-electron integrals. These can be expanded as

$$\begin{aligned} \frac{\delta (ij|kl)}{\delta x} = & (i^x j|kl) + (ij^x|kl) \\ & + (ij|k^x l) + (ij|kl^x), \end{aligned} \quad (8)$$

where  $i^x$  represents the derivative of basis function  $i$  with respect to coordinate  $x$ . The conventional method here is to compute explicitly all possible two-electron integrals in which one basis function is replaced with its derivative with respect to some coordinate. Since these integrals are more numerous than the ordinary two-electron integrals, and since evaluation and usage of the latter dominates the computation time for the energy, it is clear that direct evaluation of (8) is to be avoided if possible.

To derive the pseudospectral formulation of the energy gradient, we first review the pseudospectral assembly of the ordinary Coulomb operator,

$$J_{ij} = \sum_{kl} P_{kl} (ij|kl). \quad (9)$$

For a more complete presentation of pseudospectral Hartree–Fock theory, we refer the reader to Ref. 3.

In the pseudospectral method, the two-electron integrals (3) are not required. Instead, we compute the integrals

$$A_{kl}(g) = \int \phi_k(1) \frac{1}{r_{1g}} \phi_l(1) d\mathbf{r}_1, \quad (10)$$

where  $g$  represents a grid point in physical space. From these three-center, one-electron integrals, the physical space Coulomb operator  $J_{\text{ph}}$  is determined,

$$J_{\text{ph}}(g) = \sum_{kl} P_{kl} A_{kl}(g), \quad (11)$$

and the Coulomb operator in spectral space is recovered as

$$J_{ij} = \sum_g Q_i(g) J_{\text{ph}}(g) R_j(g), \quad (12)$$

where  $\mathbf{R}$  is the matrix of basis functions evaluated at the gridpoints, and  $\mathbf{Q}$  is the least-squares operator (see Refs. 2–3 and 5–7) given by

$$\mathbf{Q} = \mathbf{P}\mathbf{S}[\mathbf{R}^{\dagger}\mathbf{w}\mathbf{R}]^{-1}\mathbf{R}^{\dagger}\mathbf{w}. \quad (13)$$

In Eq. (13),  $\mathbf{w}$  is a diagonal matrix of grid weights, and  $\mathbf{P}$  is a projection operator (not the density matrix) for removal of dealiasing functions. The pseudospectral exchange operator has a similar form.

A useful perspective in understanding Eqs. (12) and (13) is as follows. The function  $F_j(g) = J_{\text{ph}}(g)R_j(g)$  is just the Coulomb field from the molecular charge distribution multiplied by basis function  $j$  and represented on the physical space grid  $g$ . We wish to determine the integral of this product function with a second basis function,  $i$ , to generate the matrix element  $J_{ij}$  of the Coulomb operator. One could, of course, carry out the integrals analytically; this is what is done in conventional electronic structure methods.

Instead, we compute the matrix element in two steps. First, the function  $F_j$  is expanded in a set of Gaussian basis functions (dealiasing functions). The expansion coefficients are determined by solving the weighted normal least-squares equations<sup>15</sup>

$$[\mathbf{R}^{\dagger}\mathbf{w}\mathbf{R}]c = \mathbf{R}^{\dagger}\mathbf{w}F \quad (14)$$

for  $c$ , yielding

$$c = [\mathbf{R}^{\dagger}\mathbf{w}\mathbf{R}]^{-1}\mathbf{R}^{\dagger}\mathbf{w}F. \quad (15)$$

In the second step, the matrix element of basis function  $i$  with the expansion is computed:

$$J_{ij} = \sum_k c_k \int \phi_i(1) \phi_k(1) dr_1. \quad (16)$$

The calculation of the analytic overlap integrals required to evaluate (16) is computationally trivial. The assembly of these steps into a single formula then yields Eqs. (12) and (13).

The key to obtaining high accuracy in this least-squares-fitting procedure is optimization of the grid, dealiasing, and weighting functions for each atomic basis set. These optimizations are described in some detail in Refs. 4 and 5.

Returning now to the gradient case, we examine an arbitrary term in the expansion of (7):

$$2 \sum_{ijkl} P_{ij} P_{kl} (ij|kl^x). \quad (17)$$

It would be possible to assemble this Coulomb term pseudospectrally by summing first over the indices  $k$  and  $l$ , as was done in Eqs. (9)–(12):

$$2 \sum_{ijkl} P_{ij} P_{kl} (ij|kl^x) = 2 \sum_{ij} P_{ij} \sum_g Q_i(g) R_j(g) \times \sum_{kl} P_{kl} A_{kl^x}(g). \quad (18)$$

Unfortunately, this approach would necessitate computation of one-electron integrals of the form of (10) with one basis function replaced by its derivative,

$$A_{kl}(g) = \int \phi_k(1) \frac{1}{r_{1g}} \phi_{l^x}(1) dr_1. \quad (19)$$

If instead we rewrite (17), taking advantage of the permutational symmetry of the two-electron integrals, as

$$2 \sum_{lk} P_{lk} \sum_{ij} P_{ij} (l^x k | ij), \quad (20)$$

then the pseudospectral expansion takes the form

$$2 \sum_{lk} P_{lk} \sum_g Q_{l^x}(g) R_k(g) \sum_{ij} P_{ij} A_{ij}(g), \quad (21)$$

and no new one-electron integrals are needed. The calculation now differs from the corresponding energy term only in that we need  $Q_{l^x}(g)$  rather than  $Q_l(g)$ . The assembly of the derivative Q matrix is inexpensive (relative to calculation of new integrals). It is possible to use the same fitting functions [i.e., the same R in (13)] for both the energy and gradient calculations, so that the only additional requirement for the gradient is projection of  $[R^T W R]^{-1} R^T W$  onto the set of derivative functions.

While we have shown here only a single Coulomb term, it is possible to reorder all terms of (7), Coulomb and exchange, such that the derivative function appears in Q.

An important point to note in this procedure is that there is a significant difference between finite-difference methods and the analytic evaluation of the energy derivatives as described above. The analytic formulation avoids differentiating the least-squares-fitting matrix Q with respect to the nuclear coordinates; a finite-difference technique, in contrast, would implicitly include such terms if

implemented in the most naive possible fashion (i.e., if the grid was modified in normal fashion with a nuclear perturbation). The elimination of these terms, at least to lowest order, is in practice a major advantage, as was initially hypothesized in Ref. 4. For an infinitely dense grid, these terms would in fact be zero; their contribution constitutes a spurious perturbation to the RH results (which, it should be recalled, we are attempting to mimic). The results shown below demonstrate the efficacy of this approach.

Before presenting results, it is worth discussing some of the assumptions implicit in selecting the computational scheme described above. The placement of derivative functions in the Q operator (as opposed to in the potential integrals  $A_{kl}$ ) has two advantages: (i) computationally, one avoids having to calculate a new set of potential integrals of higher angular momentum; and (ii) mathematically, it is more difficult to fit functions of higher angular momentum (which the differentiated functions generally are), and this is avoided by placing these functions in Q. However, it is by no means clear that this strategy is best, particularly if it necessitates fitting tight core orbitals instead. These issues will be explored in more detail in forthcoming publications; for now, we assert only that the procedure described here does work reasonably well.

Secondly, in this paper we use the same grid to calculate the derivatives as is used for energy evaluation. This is almost certainly not the optimal procedure; at the very least, one should reoptimize the grid for gradient calculations. Again, we plan to investigate these points in future publications.

### C. Geometry optimization

Given a method for determining the gradient, it is possible to optimize molecular geometries by iterative adjustment of nuclear coordinates so as to minimize forces. There are several techniques available for this; we chose to implement Pulay's force relaxation method.<sup>16,17</sup> In this method, Cartesian forces are transformed to internal forces by means of Wilson's B matrix,<sup>18</sup> new internal coordinates are calculated, and these are transformed back to the Cartesian frame. A guess for the second derivative matrix is required to determine the new coordinates; this is not updated. This method is clearly inferior to current state-of-the-art geometry optimization procedures, as evidenced by the large number of iterations required for convergence. However, our objective in this paper is only to demonstrate the accuracy of the final geometries obtained via the pseudospectral gradient evaluation. Subsequent publications will investigate questions of efficiency in the geometry optimization procedure.

## III. RESULTS

### A. Computational details

In Sec. III B we discuss the results of geometry optimizations performed with the pseudospectral gradient methodology as described above. In this section we present a variety of numerical data related to the calculation of the gradients themselves.

The finest grid (~900 points per atom) used in the energy calculation was also used to compute the gradients, and

the geometries were converged to more decimal places than are shown in the tables below. In particular, the convergence criterion used was that all internal forces were required to be smaller than 0.000 24 hartrees/bohr. The GAUSSIAN 82 program used a convergence criterion of 0.000 45 hartrees/bohr.

To test the rotational invariance of the pseudospectral geometries, we rotated the optimized H<sub>2</sub>CO molecule by 90° about the *y* axis (the *z* axis had been the symmetry axis) and reoptimized the geometry. The bond lengths were invariant, while the HCO bond angle changed by 0.01°. The total energies differed by 0.000 16 hartrees.

For this same molecule, the sum of the Cartesian forces in two directions is zero, while in the third direction it is 0.000 37 hartrees/bohr. The fact that translational invariance is not preserved does not affect the optimal geometries.

As a final test, we compare internal forces for the water molecule, as calculated by GAUSSIAN 82, by the pseudospectral analytic gradient method described in this paper, and by a pseudospectral finite-difference calculation. We note that, as explained in Sec. II B, the pseudospectral analytic and finite-difference calculations should not be expected to give identical results. The forces on the OH bond calculated by GAUSSIAN 82, pseudospectral analytic gradients, and finite differences were 143, 92, and 119 μhartrees/bohr, respectively. For the HOH bond angle, the corresponding forces were −218, 678, and −1890 μhartrees/rad.

### B. Geometries

Tables I and II display converged equilibrium geometries from the PS program and from GAUSSIAN 82 for 10 small molecules containing first-row atoms; a 6-31 G\*\* basis set<sup>19</sup> is used throughout. The agreement of bond lengths is

TABLE I. Comparison of optimized molecular geometries: small molecule bond lengths.<sup>a</sup>

Molecule	Bond	GAUSSIAN 82 bond length (Å)	Pseudospectral bond length (Å)	Pseudospectral error (Å)
CH <sub>2</sub>	CH	1.0988	1.0988	0.0000
H <sub>2</sub> O	OH	0.9430	0.9429	0.0001
HCN	CH	1.0589	1.0593	−0.0004
	CN	1.1328	1.1319	0.0009
HOCN	OH	0.9482	0.9475	0.0007
	CO	1.2875	1.2862	0.0013
	CN	1.1356	1.1342	0.0014
CH <sub>3</sub> F	CH	1.0828	1.0831	−0.0003
	CF	1.3646	1.3645	0.0001
NH <sub>3</sub>	NH	1.0009	1.0006	0.0003
H <sub>2</sub> N <sub>2</sub>	NH	1.0150	1.0144	0.0006
	NN	1.2155	1.2139	0.0016
H <sub>2</sub> CO	CH	1.0933	1.0931	0.0002
	CO	1.1844	1.1844	0.0000
H <sub>2</sub> O <sub>2</sub>	OH	0.9456	0.9454	0.0002
	OO	1.3957	1.3940	0.0017
HCOOH	CH	1.0851	1.0846	0.0005
	OH	0.9492	0.9489	0.0003
	CO	1.3217	1.3215	0.0002
	CO	1.1822	1.1821	0.0001

<sup>a</sup> All data are from 6-31G\*\* HF calculations.

TABLE II. Comparison of optimized molecular geometries: small molecule bond angles and torsional angles.<sup>a</sup>

Molecule	Angle	GAUSSIAN 82 bond angle (deg)	Pseudo-spectral bond angle (deg)	Pseudo-spectral error (deg)
CH <sub>2</sub>	HCH	102.9	102.9	0.0
H <sub>2</sub> O	HOH	106.0	106.1	−0.1
HCN	HCN	180.0	180.0	0.0
HOCN	HOC	111.2	111.3	−0.1
	OCN	178.4	178.6	−0.2
CH <sub>3</sub> F	CFH	109.2	109.2	0.0
NH <sub>3</sub>	HNH	107.6	107.7	−0.1
H <sub>2</sub> N <sub>2</sub>	HNN	107.6	107.9	−0.3
H <sub>2</sub> CO	HCO	122.1	122.1	0.0
H <sub>2</sub> O <sub>2</sub>	HOO	102.3	102.5	−0.2
	OCO	124.8	124.8	0.0
HCOOH	COH	108.9	109.0	−0.1
	O=CH	124.7	124.5	0.2
	HOCN	HOCN	180.0	180.0
CH <sub>3</sub> F	HCFH	120.0	120.0	0.0
H <sub>2</sub> N <sub>2</sub>	HNNH	180.0	180.0	0.0
H <sub>2</sub> CO	HCOH	180.0	180.0	0.0
H <sub>2</sub> O <sub>2</sub>	HOOH	116.2	116.5	−0.3
HCOOH	OCOH	0.0	0.2	−0.2
	HOCH	180.0	179.8	0.2

<sup>a</sup> All data are from 6-31\*\* HF calculations.

better than 0.002 Å in all cases, while that for bond angles is better than 0.3°. These results can be contrasted with the average deviation from experimental geometry for various widely used electronic structure models. For example, bond lengths of simple first-row compounds in the HF approximation with a 6-31 G\*\* basis set are typically in error by ~0.01–0.02 Å; furthermore, these average errors decrease only to 0.005 Å even with larger basis sets and at the MP3 or MP4 level of electron correlation.<sup>20</sup> Similarly, bond-angle errors are on the order of 1.0°, even when electron correlation is incorporated.<sup>20</sup> These comparisons imply that use of the PS method contributes a negligible fraction to geometry errors as compared to basis-set incompleteness and electron correlation effects.

Tables III and IV display the bond-length and bond-

TABLE III. Comparison of optimized molecular geometries: glycine bond lengths.<sup>a</sup>

Bond <sup>b</sup>	GAUSSIAN 82 bond length (Å)	Pseudospectral bond length (Å)	Pseudospectral error (Å)
N <sub>1</sub> –H <sub>6</sub>	1.0002	1.0001	0.0001
N <sub>1</sub> –H <sub>7</sub>	1.0002	1.0001	0.0001
N <sub>1</sub> –C <sub>2</sub>	1.4373	1.4341	0.0032
C <sub>2</sub> –H <sub>8</sub>	1.0853	1.0853	0.0000
C <sub>2</sub> –H <sub>9</sub>	1.0853	1.0853	0.0000
C <sub>2</sub> –C <sub>3</sub>	1.5148	1.5130	0.0018
C <sub>3</sub> –O <sub>4</sub>	1.1878	1.1875	0.0003
C <sub>3</sub> –O <sub>5</sub>	1.3288	1.3271	0.0017
O <sub>5</sub> –H <sub>10</sub>	0.9482	0.9482	0.0000

<sup>a</sup> All data are from 6-31 G\*\* HF calculations.

<sup>b</sup> Atom numbering scheme is shown in Fig. 1.

TABLE IV. Comparison of optimized molecular geometries: glycine bond angles and torsional angles.<sup>a</sup>

Angle <sup>b</sup>	GAUSSIAN 86 bond angle (deg)	Pseudospectral bond angle (deg)	Pseudospectral error (deg)
C <sub>2</sub> -N <sub>1</sub> -H <sub>6</sub>	110.6	111.0	-0.4
C <sub>2</sub> -N <sub>1</sub> -H <sub>7</sub>	110.6	111.0	-0.4
N <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub>	115.0	114.0	1.0
C <sub>3</sub> -C <sub>2</sub> -H <sub>8</sub>	107.5	108.0	-0.5
C <sub>3</sub> -C <sub>2</sub> -H <sub>9</sub>	107.5	108.0	-0.5
C <sub>2</sub> -C <sub>3</sub> -O <sub>4</sub>	125.4	124.6	0.8
C <sub>2</sub> -C <sub>3</sub> -O <sub>5</sub>	111.8	112.7	-0.9
C <sub>3</sub> -O <sub>5</sub> -H <sub>10</sub>	108.6	108.4	0.2
C <sub>3</sub> -C <sub>2</sub> -N <sub>1</sub> -H <sub>6</sub>	-58.9	-59.2	0.3
C <sub>3</sub> -C <sub>2</sub> -N <sub>1</sub> -H <sub>7</sub>	58.9	59.2	-0.3
O <sub>4</sub> -C <sub>3</sub> -C <sub>2</sub> -H <sub>8</sub>	123.1	122.8	0.3
O <sub>4</sub> -C <sub>3</sub> -C <sub>2</sub> -H <sub>9</sub>	-123.1	-122.8	-0.3
N <sub>1</sub> -C <sub>2</sub> -C <sub>3</sub> -O <sub>4</sub>	0.0	0.2	-0.2
O <sub>4</sub> -C <sub>3</sub> -O <sub>5</sub> -H <sub>10</sub>	0.0	-0.1	0.1
C <sub>2</sub> -C <sub>3</sub> -O <sub>5</sub> -H <sub>10</sub>	180.0	180.0	0.0

<sup>a</sup>All data are from 6-31 G\*\* HF calculations.

<sup>b</sup>Atom numbering scheme is shown in Fig. 1.

angle comparisons for glycine (NH<sub>2</sub>CH<sub>2</sub>COOH). The atom numbering scheme is shown in Fig. 1, and is identical to that of Ref. 21. Discrepancies here are slightly larger (e.g., one bond length is off by 0.003 Å) but are still quite acceptable. These discrepancies can in fact be significantly reduced by further optimization of grids and dealiasing sets. Such work will be reported in a future communication.

Finally, Table V shows total energies for the 11 molecules tested here, as calculated by each program at its own optimized geometry. The PS and RH results are within 0.1 kcal/mol in every instance, as was the case in our previous studies<sup>5-7</sup> (in which we compared energies at fixed geometries).

#### IV. CONCLUSION

We have shown that pseudospectral Hartree-Fock methods are capable of yielding equilibrium geometries for compounds composed of first-row atoms which agree quantitatively with those obtained from conventional Hartree-Fock programs. Glycine, in particular, is a reasonably demanding test case, and the accurate computation of the torsional angles for this system suggests that the PS method will

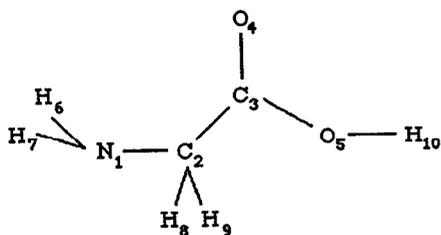


FIG. 1. Glycine molecule.

TABLE V. Comparison of optimized molecular geometries: total energies.<sup>a</sup>

Molecule	GAUSSIAN 82 energy <sup>b</sup> (hartrees)	Pseudo- spectral energy <sup>c</sup> (hartrees)	Pseudo- spectral error (hartrees)
CH <sub>2</sub>	-38.876 308	-38.876 270	0.000 038
H <sub>2</sub> O	-76.023 615	-76.023 628	-0.000 013
HCN	-92.877 138	-92.877 097	0.000 041
HOCN	-167.729 022	-167.729 144	-0.000 122
CH <sub>3</sub> F	-139.039 736	-139.039 646	0.000 090
NH <sub>3</sub>	-56.195 545	-56.195 552	-0.000 007
H <sub>2</sub> N <sub>2</sub>	-110.001 231	-110.001 301	-0.000 070
H <sub>2</sub> CO	-113.869 743	-113.869 862	-0.000 119
H <sub>2</sub> O <sub>2</sub>	-150.776 965	-150.777 115	-0.000 150
HCOOH	-188.770 566	-188.770 665	-0.000 099
Glycine	-282.848 342 <sup>d</sup>	-282.848 215	0.000 127

<sup>a</sup>All data are from 6-31 G\*\* HF calculations.

<sup>b</sup>Total energy at GAUSSIAN 82 optimized geometry.

<sup>c</sup>Total energy at pseudospectral optimized geometry.

<sup>d</sup>Glycine optimized with GAUSSIAN 86 rather than GAUSSIAN 82.

be quite suitable for studying conformations of complicated organic molecules.

A great deal of work remains to be done in developing a complete PS geometry optimization scheme. One approach we are currently pursuing is to use a much less expensive grid and dealiasing set for most of the gradient steps, employing accurate parameters only for the last few iterations. If roughly 10-15 steps are required for optimization, an overall savings of a factor of 2-4 in CPU time could be realized. This additional factor, when multiplied by the previously documented improvements for single-point calculations (a factor of 10 for glutamine), would result in an overwhelming advantage for the PS approach, one which further modification of conventional programs would be extremely unlikely to overcome. Furthermore, additional improvements in the basic algorithms of the PS method and optimization of grid and dealiasing parameters will continue to produce CPU reductions and accuracy increases for some time to come.

Extensions of the methodology to other atoms and to correlated calculations is currently in progress. GVB gradient calculations will be reported shortly, and appear to yield a level of accuracy similar to that presented here. A method for calculating atomic charges from the pseudospectral electrostatic potential has been developed and will be reported in a subsequent paper. Optimization of grid and dealiasing parameters for second-row atoms and transition metals is a tedious but tractable task which is proceeding successfully. Second-derivative PS methods, involving solution of the coupled perturbed HF equations, are also underway.

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