

New pseudospectral algorithms for electronic structure calculations: Length scale separation and analytical two-electron integral corrections

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We describe improved algorithms for carrying out pseudospectral Hartree–Fock calculations; these algorithms are applicable to other *ab initio* electronic structure methodologies as well. Absolute energies agree with conventional basis set codes to within 0.25 kcal/mol, and relative energies agree to better than 0.1 kcal/mol for a wide variety of test molecules. Accelerations of CPU times of as large as a factor of 6.5 are obtained as compared to GAUSSIAN 92, with the actual timing advantage increasing for larger basis sets and larger molecules. The method is shown to be highly reliable and capable of handling extended basis sets.

I. INTRODUCTION

During the past several years, our research groups at Columbia, Caltech, and Schrödinger, Inc. have continued to develop a new approach to solving *ab initio* electronic structure equations which involves the use of both numerical grids and analytical two-electron integrals.^{1–5} The basic algorithm that we employ is similar in structure to pseudospectral methods, widely used in hydrodynamic simulations^{6–10} and also in a variety of chemical physics applications, e.g., scattering theory and calculation of vibrational wave functions.^{11–14} In these methods, one uses both a numerical grid and a basis set; in our case, the latter consists of standard quantum chemical contracted Gaussian basis sets. However, the details required to make such a method efficient for the specialized requirement of electronic structure calculations are highly significant; the methods we have developed are best thought of as a synthesis of many numerical technologies with complicated interconnections.

There have been major advances in electronic structure methodology over the past few years; two-electron integral generation schemes have become much more efficient [GAUSSIAN 92 (Ref. 15) is perhaps 100 times faster than GAUSSIAN 86 for large molecules] and density functional theory and the associated computer codes have become much more accurate and reliable.^{16–24} While we focus in this paper on single point Hartree–Fock calculations, the basic numerical technology described here is applicable to both density functional and wave function based electron correlation methods; results for these methods will be presented in subsequent publications, as will those for analytical gradient methodologies. Here our concern is the optimal ways of evaluating the Coulomb and exchange energies which arise

in any first-principles electronic structure method.

The use of numerical grid-based methods is significantly less developed in molecular electronic structure theory than conventional two-electron integral technology, which has benefitted from the large number of man-years expended investigating these problems over the past 20 years. However, this situation is changing rapidly, due in part, to the increasingly impressive performance available from density functional methods, where parts of the calculation have to employ numerical integration. We believe that, as greater effort is expended, the value of such methods will become clear and that there will be a convergence in all electronic structure codes in which numerical and analytical methods are intermixed. The key issues are then how to accomplish this admixture without sacrificing the high degree of reliability that is present in analytical two-electron codes like GAUSSIAN 92.

In this paper we present two new algorithmic strategies which substantially reduce the number of grid points per atom required to achieve accurate relative energies and total energies for calculations on large molecules. The first is to employ a larger number of analytical integrals in the assembly of the Coulomb and exchange operators. The development of efficient new schemes for the evaluation of two-electron repulsion integrals (ERI's) has significantly reduced the computational effort required per integral, in part by reducing operation counts and in part by achieving better performance from vector hardware by reorganization of data structures. As we utilize only two-center and a selected set of three-center ERI's, the number of integrals to be evaluated in our formalism is orders of magnitude less than in conventional electronic structure codes. At the same time, this small subset of integrals includes the largest (by at least an order of magnitude) terms in the electrostatic energy; we are therefore able to substantially reduce the number of grid points that we

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employ, as the precision required of the numerical integration scheme to achieve equivalent accuracy decreases accordingly. The overall scheme for utilizing two-electron corrections to the pseudospectral calculations will be referred to as the two-electron correction (TEC) algorithm in what follows.

The second strategy, which we shall refer to as a length scales (LS) algorithm, involves sorting basis functions according to the size of the smallest exponent. We have generally observed that projecting the pseudospectral Fock operator onto a basis function is much more accurate if that basis function has a large exponent [i.e., is a short range (SR) function], in part because one can then restrict the domain over which the least squares fit is carried out, as has been described previously. In the case where one of the two Fock matrix indices is a short range function, this strategy can be implemented trivially. When both functions are long range (LR), however, more effort is required; we later describe an algorithm which works efficiently in this case as well.

Once the basic algorithms have been coded, it is necessary to design a control structure which adjusts the usage of two-electron integrals as a function of iteration number (in general, smaller integrals need only be calculated on the most accurate iterations). Then, grids and dealiasing sets must be developed which take advantage of the LS and TEC algorithms in an efficient fashion. The entire scheme then has to be tested with regard to accuracy and efficiency on a large number of molecules and molecular conformations.

The paper is organized as follows. Section II provides a very brief overview of the development of the pseudospectral (PS) formalism up to the present time; details can be found in previous papers. In Secs. III and IV, we present the formalism associated with the LS and TEC algorithms, respectively. Section V describes the detailed implementation of these methods, including grid and dealiasing optimization and development of iteration sequences. Section VI presents accuracy and timing tests, comparing our results with those obtained from GAUSSIAN 92. Section VII, the conclusion, discusses future algorithmic improvements.

In previous papers, we have emphasized agreement with analytical methods of the total energy, typically achieving a 0.1 kcal/mol level of agreement. However, in reality, the only relevant quantities are total energy differences. By relaxing the constraint on such close agreement of the total energy (particularly for large molecules) but insisting on maintaining agreement for relative energies (easily tested by studying a series of molecular conformations), we are able to make significant reductions in our computational effort. This parameter set displays very small total energy deviations (less than 0.25 kcal/mol) from GAUSSIAN 92 for the small and medium-size molecules we report in this paper (the largest is porphine, with ~ 40 atoms). However, for larger molecules like C_{60} , a tighter parameter set is required to achieve this sort of agreement; discrepancies can be as large as several kcal/mol for the default parameter set. We note that Gaussian itself must use its own tight parameter set, at a very large cost in CPU time, to converge C_{60} , and that other numerical methods (e.g., those in commercial density functional codes) simply have not been tested with regard to the accuracy of

energies for molecules of this size. Thus, in dealing with large molecules the requirements for accuracy become *qualitatively* different and tests on small molecules are in no way sufficient to guarantee the accuracy of relative energies in the large molecule regime. We shall discuss these issues in detail in a subsequent paper.

II. PSEUDOSPECTRAL ASSEMBLY OF COULOMB AND EXCHANGE OPERATORS

In conventional electronic structure theory, the Coulomb and exchange operators have the form

$$J_{ij} = \sum_{kl} (ij|kl) \rho_{kl}, \quad (1)$$

$$K_{ij} = \sum_{kl} (ik|jl) \rho_{kl}, \quad (2)$$

where $(ij|kl)$ is a two-electron repulsion integral over atomic basis functions and ρ is the density matrix. Pseudospectral methods are based upon representing a two-electron integral $(ij|kl)$ as a quadrature over grid points:

$$(ij|kl) = \sum_g Q_i(g) R_j(g) A_{kl}(g), \quad (3)$$

where $R_j(g)$ is an atomic basis function j evaluated at a grid point g , and

$$A_{kl}(g) = \int \frac{R_k(g') R_l(g')}{|g - g'|} dg' \quad (4)$$

is a three-center, one-electron integral (potential integral) representing the field at g due to the product charge distribution of basis functions R_k and R_l .

The matrix $Q_i(g)$ is a least squares fitting operator which is designed to fit any right-hand side $R_j(g) A_{kl}(g)$ in the region of space relevant to atomic basis function $|i\rangle$. If $|i\rangle$ is a short range function, this is done by specifying a local fitting basis for each atom, solving the normal equations defined by the fitting basis and the numerical grid, and projecting the resultant expansion onto $|i\rangle$ via analytical overlap integrals of the fitting basis with $|i\rangle$. The mathematical details of this procedure have been given in several papers and we shall not repeat them here. For our purposes, one can think of $Q_i(g)$ as a set of quadrature weights that are specially designed to provide accurate integration over the function $|i\rangle$. Because of this special design, the accuracy of the result for a given number of grid points is necessarily much better than for a generic quadrature scheme (e.g., Gaussian quadrature) unless there are instabilities in the fitting procedure. From long experience, we have been able to control the instabilities by a variety of techniques so that the algorithm provides a robust performance for arbitrary molecules.

Because of the projection onto analytical overlap integrals, our method reduces to the analytical result in the limit that the quadrature scheme becomes exact. This can be accomplished either by making the fitting basis complete with respect to the right hand side or by making the underlying

quadrature on the grid exact (in the latter case, one of course would not need to use the fitting basis). In practice a combination of the two approaches is used to make the PS results very close, but not identical to, those obtained from analytical theory.

When $|i\rangle$ is a long range function, the least squares fit has to be carried out over a large portion of the molecule. This leads to a significant loss of accuracy for a fixed number of grid points as well as greater computational expense in assembling the collocation matrix and solving the normal equations. The length scales algorithm described below is designed to deal with this problem.

Substituting Eq. (3) into Eq. (1) leads to the following PS expressions for J and K :

$$J_{ij} = \sum_g Q_i(g) J(g) R_j(g), \quad (5)$$

where the physical space Coulomb operator $J(g)$ is given by

$$J(g) = \sum_{kl} A_{kl}(g) \rho_{kl}, \quad (6)$$

$$K_{ij} = \sum_g Q_i(g) K_j(g), \quad (7)$$

and

$$K_j(g) = \sum_k A_{jk}(g) \sigma_k(g) \quad (8)$$

is the pseudospectral physical space exchange field. The intermediate quantity $\sigma_k(g)$ is defined as

$$\sigma_k(g) = \sum_l R_l(g) \rho_{kl}. \quad (9)$$

These are the equations used in our electronic structure package, PS-GVB, prior to the methods presented here. As noted before, the formal scaling of these equations is N^3 (where N is the basis set size) and with the use of integral cutoffs this becomes N^2 .

III. LENGTH SCALE ALGORITHM

A. Overview

In previous papers, we have shown that the accuracy of pseudospectral Fock matrix elements is highly dependent upon the ordering of the basis functions: it is best to fit diffuse functions and project onto short range functions. However, the structure of the Coulomb and exchange operators makes it difficult to enforce this prescription at all times.

We have worked out a way of doing this at a relatively small computational cost. Essentially, one never projects onto a diffuse function unless all three of the functions in $R_j(g)A_{kl}(g)$ are also diffuse functions. In the latter case, the fitting matrix does not need to contain tight functions and, hence, is inexpensive to assemble despite being extended over the entire molecule. This length scale algorithm is a crucial complement to the increased utilization of analytical integrals described below. When we employ the very small

grids (~ 100 points/atom) of the present paper, the use of length scales improves the energy by an order of magnitude with perhaps a 10–20 % increase in CPU time.

We wish to calculate elements of the Fock matrix for the Coulomb and exchange operators, avoiding the use of diffuse functions (e.g., $3s$ and $3p$ functions for a first row DZP basis; in the general case one can sort any basis set into short and long range functions by examining the smallest exponent of each basis function) in the least squares fitting operator. If one of the indices in the Fock matrix element F_{ij} (either i or j) is a nondiffuse function, the algorithm is trivial: one simply selects that function as the one lying on the left-hand side. In Eqs. (5) and (7), for example, one simply requires that the index i is a short range function. Note that in the PS formulation $J_{ij} \neq J_{ji}$, unless the quadrature scheme is exact. Difficulties arise when both i and j are diffuse functions. At first glance, it would seem as though this problem was intractable, i.e., that one of the two diffuse functions would have to be used in the least squares operator. As is shown later, however, this is not the case, albeit at some additional computational cost.

B. Coulomb operator

The key to a consistent length scale formulation is to use the symmetry of the two-electron integrals to rewrite the pseudospectral expressions for the Coulomb matrix elements. An alternative formulation for J_{ij} is

$$J_{ij} = \sum_{g=1}^{N_g} A_{ij}(g) B(g), \quad (10)$$

where $B(g)$ is a quantity analogous to the Coulomb field but without the integration over the kernel r_{12}^{-1} :

$$B(g) = \sum_{kl} Q_k(g) R_l(g) \rho_{kl}, \quad (11)$$

where ρ_{kl} are elements of the density matrix. It is straightforward to show that Eq. (10) is equal to the usual two-electron integral expression for the Coulomb operator [or to Eq. (1) in the limit that the quadrature scheme becomes exact].

Starting from Eq. (10), it is now possible to construct a more complex scheme in which Q_k in Eq. (11) is never a diffuse function unless R_l is also a diffuse function. In this case, the entire function to be fit via the least squares operator contains *only* long wavelength behavior and, consequently, is relatively easy to integrate, even on a sparse grid. Furthermore, a small fitting basis containing only diffuse functions can be employed in this case, thus greatly ameliorating the problem of the growth of the matrix that has to be inverted in solving the normal equations.

We now explicitly consider the assembly of spectral Coulomb matrix elements J_{ij} , where i and j are both long range functions, using the length scales algorithm. For the present purposes, we assume only two length scales, which correspond for first row atoms to $3sp$ functions (long range) and all remaining functions ($1s, 2sp, 3d$) designated as short

range. We first define a modified version of $B(g)$, which in the limit of exact quadrature is entirely equivalent to Eq. (11):

$$\begin{aligned}
 B(g) = & \sum_{k=SR} \sum_{l=SR} Q_k(g) R_l(g) \rho_{kl} \\
 & + 2 \sum_{k=SR} \sum_{l=LR} Q_k(g) R_l(g) \rho_{kl} \\
 & + \sum_{k=LR} \sum_{l=LR} Q_k(g) R_l(g) \rho_{kl}. \quad (12)
 \end{aligned}$$

The critical feature of this formulation is that it contains no terms in which R is short range and Q is long range. Thus, when used in Eq. (10) for both i and j long range, the long range Q operator is used only if the three remaining indices in the two electron integral are long range as well. There is an additional computational cost in this algorithm in the assembly of $B(g)$, but the final calculation of J_{ij} in Eq. (10) replaces an equally costly evaluation of $Q_i J(g) R_j$ in the standard ordering. The $B(g)$ assembly cost can be reduced by using quantities that have already been evaluated for the ordinary pseudospectral exchange operator and by using cutoffs.

C. Exchange operator

A similar methodology can be used to implement length scales in the evaluation of the exchange operator. As before, if either i or j is an short range function, K_{ij} can be computed by choosing the appropriate ordering in Eq. (3); thus, difficulties again arise only if both i and j are long range. In this case, we define a modified "short range" exchange field $K_j^{(SR)}(g)$ as

$$K_j^{(SR)}(g) = \sum_{k=SR} A_{jk}(g) \sigma_k^{(SR)}(g) + 2 \sum_{k=LR} A_{jk}(g) \sigma_k^{(SR)}(g), \quad (13)$$

where the intermediate quantity $\sigma_k^{(SR)}(g)$ is given by

$$\sigma_k^{(SR)}(g) = \sum_{l=SR} Q_l(g) \rho_{kl}. \quad (14)$$

This field includes terms containing one or two short range functions; in every term, a short range Q is employed. Note that, in contrast to the usual intermediate σ field, the modified $\sigma^{(SR)}$ field is formed from Q operators and the density matrix, as opposed to the R operators used in ordinary PS theory.

The modified long range exchange field $K_j^{(LR)}(g)$ is

$$K_j^{(LR)}(g) = \sum_{k=LR} A_{jk}(g) \sigma_k^{(LR)}(g), \quad (15)$$

where $\sigma_k^{(LR)}(g)$ is given by

$$\sigma_k^{(LR)}(g) = \sum_{l=LR} R_l(g) \rho_{kl}. \quad (16)$$

Here we revert to the usual formulation of σ except that the sum is restricted to be over long range functions only.

K_{ij} is then obtained by projecting the modified exchange fields onto the appropriate complementary operator as

$$\begin{aligned}
 K_{ij} = & \frac{1}{2} \left(\sum_g K_j^{(SR)}(g) R_i(g) + \sum_g K_i^{(SR)}(g) R_j(g) \right) \\
 & + \sum_g K_j^{(LR)}(g) Q_i(g). \quad (17)
 \end{aligned}$$

Decomposition of Eq. (17) into individual terms and comparison with the full set of pseudospectral terms required to represent K_{ij} reveals that every individual term is contained in Eq. (17) and that the only terms which require the use of a long range Q operator, represented in the third sum in Eq. (17), are those where the remaining three indices are also long range. Thus, the above formulation successfully accomplished the desired task, namely the use of short range least squares fitting matrices wherever possible.

IV. TWO-ELECTRON INTEGRAL CORRECTIONS

A. Overview

From an early point in its development, PS-GVB has utilized analytical integrals for one-center Coulomb and exchange terms. These terms are small in number and their evaluation analytically is obviously trivial; hence, the computational cost of this strategy is virtually nonexistent. Accuracy of the total energy is typically increased by one to two orders of magnitude as compared to a fully pseudospectral calculation for a grid of 1000 points/atom.

The development of very fast recursive two-electron integral algorithms has now proceeded to the point where the calculation of additional integrals analytically is worthwhile. The basic idea is to order the integrals into classes and calculate analytically only the largest terms. If these are a sufficiently small fraction of the total number of integrals (which can be enforced by the use of cutoffs), the CPU time required is essentially negligible and permits a threefold to fivefold reduction in grid size for a comparable level of accuracy. The scheme described below can be improved upon and further reductions in computational effort will be possible.

In this paper we only consider utilization of integrals with at least one common product center, i.e., of the form $(aa'|bc)$, where a and a' are (possibly different) basis functions on the same atom (atom A) and b and c are basis functions on atoms B and C, respectively. Besides restricting the number of integrals, the common product center renders the calculation of individual integrals less expensive, as described later.

For the Coulomb operator, a justification of this strategy is straightforward. Examination of statistics for the size of density matrix elements indicates that those in which both indices are valence functions on the same center are 100 or more times larger than those for which the indices are on different atoms or for which one index is a polarization function. This observation follows from the well-known fact that

electron densities in molecules are small perturbations on those in an atom. Hence, terms of the form $(ab|cd)$ where the pairs (a,b) and (c,d) are both on different atoms, contribute 10 000 times less amplitude to the Coulomb energy.

For exchange, the situation is not so clearcut and we are still attempting to formulate a rigorous theoretical basis for sorting terms. In practice, we have chosen to include only two-center analytical integrals in assembly of the exchange operator, on the basis of empirical experimentation with the effects of three-center terms. This approximation works quite well in practice and, in fact, can be restricted to nearest-neighbor two-center terms for many of the self-consistent iterations (those where only ~ 0.01 – 0.001 a.u. accuracy is required). However, we believe that inclusion of a limited set of three-center terms will prove useful and intend to evaluate this in the future.

Several technical considerations have played an important role in the development of the scheme presented below. First, the terms to be computed analytically must be subtracted from the pseudospectral operators to avoid double counting. For an arbitrary set of two-electron integrals, the subtraction procedures is nontrivial and indeed easily could be considerably more expensive to implement than the Fock matrix assembly itself. Consequently, it is important to carry out analytical corrections on groups of terms which can be replaced with relatively little effort in the pseudospectral assembly scheme.

A second feature of the methodology is the use of overlap integrals to estimate the size of terms when considering whether to compute them analytically or numerically. Cutoff thresholds are established and terms whose estimators are below these thresholds are either done numerically or neglected entirely. This allows a considerable reduction in CPU time as compared with having to analytically evaluate the entire class of terms.

To calculate the integrals, we have written a version of the Gill–Head–Gordon–Pople algorithm²⁵ (currently implemented in GAUSSIAN 92) specialized to the evaluation of integrals sharing an atomic center. The modifications of the algorithm to achieve efficiency for these special cases is straightforward and is briefly described later.

We describe here the implementation of two- and three-center corrections for the standard pseudospectral formulas. If the length scales algorithm is being used simultaneously, one has to subtract off the appropriate part of these terms as well. While this is not presented in detail below, and does involve a fair degree of complexity, it can be worked out using the basic approach described here, and the computational expense is comparable to that for the corrections which are presented later.

B. Coulomb corrections

For the Coulomb operator, we consider the following types of two-electron integrals for analytical corrections: (1) One-center terms of the form $(aa'|a''a''')$; (2) two-center terms of the form $(aa'|bb')$; (3) two-center terms of the form $(ab|a'b')$; (4) two-center terms of the

form $(aa'|a''b)$; (5) three-center terms of the form $(aa'|bc)$. Here a , b , and c represent atomic basis functions on atoms A, B, and C, respectively.

A crude way to assess the importance of each class of terms is to assign a value of 1 to density matrix elements for occupied orbitals on the same atom and δ for all other density matrix elements. In the expression for the Coulomb energy, terms (1) through (5) are multiplied by the following density matrix elements:

- (1) $\rho_{aa'}\rho_{a''a'''}$,
- (2) $\rho_{aa'}\rho_{bb'}$,
- (3) $\rho_{ab}\rho_{a'b'}$,
- (4) $\rho_{aa'}\rho_{a''b}$,
- (5) $\rho_{aa'}\rho_{bc}$.

Assuming that all of the functions are occupied orbitals, this leads to an approximate magnitude for each class of terms as $\mathcal{O}(1)$: terms 1,2; $\mathcal{O}(\delta)$: terms 4,5; $\mathcal{O}(\delta^2)$: term 3. This leads to the following strategy (which must be tested empirically). Terms of the form (1) and (2) should be done analytically for all atoms A and all pairs a and b . Notice as well that there is virtually no falloff in the size of the integrals in class (2) as a function of the a – b separation distance, hence, no distance cutoffs are employed here. Terms of the form (4) and (5) are done analytically provided the overlap of the function pair lacking a center coincidence [$a''b$ in (4), bc in (5)] is greater than a specified threshold. The threshold is adjusted empirically to yield acceptable molecular properties in a given overall pseudospectral scheme and, hence, will be a function of the grid, dealiasing scheme, etc. The cutoffs are actually applied to blocks of integrals (e.g., a $2p$ – $2p$ block, containing nine different bc function pairs) and utilize pseudooverlaps computed by averaging the absolute values of the individual overlap integrals in the block and dividing by the number of integrals.

Terms of the form (3) are likely to be important only for atoms in close physical proximity. Consequently, we employ here a simple distance cutoff in which analytical corrections for these terms are carried out provided the distance between atoms a and b is less than a specified tolerance. This may not be optimal (perhaps different functions on the atoms should be treated differently) but leads to reasonable results as shown below.

When a or a' is a polarization function in an aa' pair, the magnitude of the corresponding density matrix element is considerably diminished. For (1) and (2), the cost of computing the analytical integrals is essentially trivial and we ignore this effect. For (4) and (5), we set the cutoff threshold on the bc overlaps differently for this case than for the case where both a and a' are occupied. The two cutoffs are empirically adjusted on a set of test molecules to yield reliable energies and other properties.

Having constructed our correction scheme, we must now devise efficient algorithms for implementing the pseudospectral subtractions. We define two types of restricted Coulomb operators to be subtracted from the full operator in differing specific cases: J_A , in which sums are over functions a, a' that are both on the same atom, and J_S , in which only terms where the absolute value of the overlap integral of the two

basis functions is greater than a given threshold is included:

$$J_A(g) = \sum_{aa'} A_{aa'}(g) \rho_{aa'}, \quad (18)$$

$$J_S(g) = \sum_{S_{kl} > S_{\min}} A_{kl}(g) \rho_{kl}. \quad (19)$$

Note that the sum in Eq. (18) extends over all atoms in the molecule.

Two versions of J_A and J_S are constructed. For J_A , one term includes polarization functions and one does not. For J_S , two different thresholds S_{\min} are defined, one of which, S_1 , is to be used when a polarization function is involved and the other, S_2 , which is used when no polarization function is involved (the usage of J_A and J_S are described later). The computational cost of assembling these three operators is identical to that for evaluating a single operator, as partial sums can be constructed and then added into the appropriate term.

Once the four operators are constructed, the final assembly of the spectral Coulomb matrix is carried out with the appropriate operator, i.e., one in which the terms to be computed analytically are subtracted from the pseudospectral evaluation of matrix element, so as to avoid double counting. For example, in the evaluation of a Coulomb matrix element $J_{aa'}$ between two occupied orbitals a and a' , we would subtract operator J_{S_1} if a or a' is a polarization function:

$$J_{aa'} = \sum_g Q_a(g) [J(g) - J_{S_1}(g)] R_{a'}(g). \quad (20)$$

If neither a or a' is a polarization function, Eq. (20) would be used with J_{S_2} replacing J_{S_1} . Similarly, if functions b and c are on different atoms B and C, we would subtract either J_{A_1} , J_{A_2} , or nothing, depending upon the size of the overlap integral S_{bc} .

The principal reason for the use of these cutoffs is to limit the number of three-center, two-electron integrals of the form $(aa'|bc)$ that must be evaluated analytically. The same criteria involving the overlap integrals S_{ij} are implemented in the two-electron integral code and only terms satisfying the criteria (e.g., for an $(aa'|bc)$ integral with a, a' not polarization functions, $S_{bc} > S_1$) are evaluated.

The above algorithm deals with all relevant terms above except for those of the form $(ab|a'b')$. In this case, one must compute a "diatomic" Coulomb correction matrix via the equation:

$$J_{ab}^{(D)} = \sum_g Q_a(g) J_D(g) R_b(g) \quad (21)$$

where the diatomic pseudospectral Coulomb field $J_D(g)$ is defined by

$$J_D(g) = \sum_{ab} A_{ab}(g) \rho_{ab} \quad (22)$$

the sum being restricted to functions a on atom A, b on atom B.

While $J_D(g)$ itself does not involve extra computation (it can be formed as an intermediate step in ordinary Coulomb assembly), assembly of the correction matrix $J_{ab}^{(D)}$ in Eq. (21) is additional work. $J_{ab}^{(D)}$ is then subtracted from the usual J_{ab} . Fortunately, for most iterations in the PS scheme, corrections of this type can be restricted to atom pairs that are nearest neighbors.

C. Exchange corrections

For exchange, an analysis of the density matrix elements analogous to that given earlier for the Coulomb operator yields, for cases (1)–(5), $\mathcal{O}(1)$: terms 1,3; $\mathcal{O}(\delta)$: term 4; $\mathcal{O}(\delta^2)$: terms 2,5. This suggests that we treat only two-center terms analytically for exchange. Some compelling reasons for this are (1) corrections for the three-center terms of the fifth case are quite expensive; also, there is no reason to believe that these terms are smaller than many four center terms; (2) a simple distance cutoff can be used. The correction procedure involves calculation of a "diatomic" \mathbf{K} matrix $K_{ab}^{(D)}$:

$$K_{ab}^{(D)} = \sum_g Q_a(g) K_b^{(D)}(g), \quad (23)$$

where

$$K_b^{(D)}(g) = \sum_{k \in \{a,b\}} A_{bk}(g) \sigma_k(g) \quad (24)$$

is the pseudospectral physical space exchange field for the diatomic AB pair and the intermediate quantity $\sigma_k(g)$ is defined as

$$\sigma_k(g) = \sum_{l \in \{a,b\}} R_l(g) \rho_{kl}. \quad (25)$$

The sum over l again being restricted to functions on atoms A or B.

Once $K_{ab}^{(D)}$ is computed, it can be subtracted from the usual pseudospectral \mathbf{K} matrix. Again, distance cutoffs are used to restrict the exchange corrections (which do involve extra work) to a small subset of atom pairs.

D. Recursive two-electron integral codes

We utilize the recursive two-electron integral algorithms developed by Gill, Head-Gordon, and Pople. As these authors have presented their formalism in detail in Ref. 25, we will not review it here, focusing instead upon the modifications which provide additional efficiency for the special cases in which either the pair of basis functions in the bra or the ket in the BRAKET algorithm share a common center. This is the case in all of the integrals we utilize with the exception of those of the form $(ab|a'b')$; as these are computed only for atom pairs within the distance cutoff (reducing a formal N^2 scaling to a constant factor), for they contribute a negligible amount to the overall computation time for large molecules.

A trivial modification of the algorithm when there is a center coincidence is to avoid recursive steps involving multiplication by zero. There are numerous instances in which

the distance between the function centers of the bra or ket pair appears as a multiplicative constant in the algorithm; these steps can easily be eliminated.

A more drastic simplification is possible when the distance between the bra and ket product center multiplied by the exponent of the primitive Gaussian is large, i.e., when the charge distributions can be treated as interacting classically (see. Ref. 25 for details of when the "classical" approximation is valid). In this case, if there is a center coincidence, the recursive formulas are independent of the Gaussian exponents of the primitives as the initial recursive function $[0]^{(m)}$ (using the notation of Ref. 25) has reached an asymptotic (large) value. One can then calculate the recursion out to a certain point (the $[r]^{(0)}$ functions depend on the $[0]^{(m)}$ functions in a way that again renders them independent of exponent) for the generic asymptotic value without having to redo the calculation for each pair of primitive Gaussians on the coincident center. As there are no cutoffs if both primitives are on the same atom, this will be considerable number of pairs, e.g., 21 pairs just for an $1s-1s$ bra or ket in a 6-31G** basis. Coding this efficiently is nontrivial because one has to sort the classical and nonclassical primitives in a systematic fashion to preserve the vectorization of the BRAKET algorithm; our solution to this problem is at present significantly nonoptimal and we expect that future versions of PS-GVB will have substantially improved CPU times for two-electron integral generation as this algorithm is optimized.

V. CODE AND PARAMETER SET OPTIMIZATION

A. Overview

The basic algorithmic structure described earlier is, in principle, enormously flexible, allowing various terms in the Hamiltonian to be treated at different levels of numerical accuracy (and, concomitantly, at different costs of CPU time). This complex structure requires control parameters to manage the choices (e.g., of which integrals will be done analytically and which numerically); optimal values of these choices change as a function of iteration number as well. Finally, the detailed implementation of the different integral computations is itself highly nontrivial and improvements in performance are available from a number of different strategies.

We first describe the key control parameters which determine the basic structure of a given iteration, these include the two-electron integral cutoffs for both Coulomb and exchange corrections and choice of numerical grid. We then present our empirically determined iteration sequence, designed to generate reliable relative energies for the vast majority of molecules.

The program contains a substantial number of parameters that are not described later, for example, those controlling the accuracy of the one- and two-electron integrals, or the thresholds for eliminating them completely. These are not really relevant to the basic issues addressed in this paper: implementation and performance of the TEC and LS algorithms. Discussions of these parameters can be found in the PS-GVB users guide.

B. Control parameters

1. Grids and fitting basis

The most important parameter for any iteration is the grid parameter. We have optimized three types of grids: F is fine (~ 300 points/atom), M is medium (~ 100 points/atom) and C is coarse (~ 70 points/atom). Optimization is carried out for a series of small molecules for each atom for a given basis set and then tested for accuracy on a larger list of molecules. Finally, the performance is evaluated by computing energy differences for various conformational states of several molecules. Each grid has associated with it a dealiasing file of fitting functions which is optimized along with the grid.

The grids are atom centered, consisting of spherical shells with the points arranged according to the quadrature schemes of Lebedev which exactly integrate spherical harmonics up to a certain order. Atomic grids are synthesized into a molecular grid by truncating the grid at the Voronoi surfaces of each atom, with a Lagrange interpolation scheme to insure smooth assignment of grid weights as a function of molecular geometry. Our grid generation scheme has been described in detail in a previous paper.²⁶ The major modification we have made here is that the position of each radial shell is individually optimized and the angular point distribution of each shell is also optimized. The latter feature permits considerably better performance for small grids.

The grid sizes used here are 2–3 times smaller than those used in the previous version of PS-GVB. This is a consequence of the use of analytical corrections, which remove the largest part of the Coulomb and exchange operators from the grid. Further reduction of the grid would in fact be possible were it not for difficulties that arise due to the transformation from atomic orbitals to molecular orbitals. Standard electronic structure basis sets typically contain a few small eigenvalues in the overlap matrix, on the order of 10^{-3} – 10^{-4} . Matrix elements of the canonical molecular orbitals associated with these eigenvalues are very sensitive to errors in the corresponding AO matrix elements because the transformation coefficients are very large. As these basis functions invariably make very small contributions to the energy (indeed, such contributions are much smaller than those left out due to basis set incompleteness), it should, in principle, be possible to remove these functions with no loss of chemical accuracy. We have implemented a scheme to remove canonical functions via a projection operator which works reasonably well for the smallest eigenvalues. However, this is not a complete solution to the problem and other strategies should result in superior performance.

In Tables I, II, and III we present grid generation parameters for atoms in the first two rows for the coarse, medium, and fine grids, respectively. The angular structure of the grid utilizes point distributions developed by Lebedev; we indicate the number of points in each radial shell in the table which suffices to uniquely specify the appropriate Lebedev grid. The shell positions and Lebedev order for each shell have been optimized empirically.

The dealiasing, or fitting basis is used in the least squares fitting procedure to expand the pseudospectral Fock

TABLE I. Coarse grid generation parameters.

| Atom | Radial shell position (bohr) | Points/Shell |
|-----------|------------------------------|--------------|
| H | 0.100 00 | 6 |
| | 0.446 35 | 12 |
| | 0.845 46 | 14 |
| | 1.407 77 | 12 |
| | 2.179 98 | 12 |
| | 3.750 00 | 6 |
| | 4.500 00 | 6 |
| | | |
| Li | 0.142 94 | 6 |
| | 0.714 70 | 8 |
| | 1.429 41 | 12 |
| | 2.687 91 | 20 |
| | 4.407 27 | 26 |
| | 6.572 12 | 20 |
| | 8.806 37 | 12 |
| | 11.841 18 | 8 |
| 14.801 48 | 6 | |
| C | 0.071 12 | 6 |
| | 0.355 62 | 8 |
| | 0.711 25 | 12 |
| | 1.337 46 | 20 |
| | 2.192 98 | 12 |
| | 3.270 18 | 12 |
| | 5.000 00 | 6 |
| | 9.000 00 | 6 |
| N | 0.071 12 | 6 |
| | 0.355 62 | 8 |
| | 0.711 25 | 12 |
| | 1.337 46 | 20 |
| | 2.192 98 | 12 |
| | 3.270 18 | 12 |
| | 4.381 91 | 8 |
| | 5.891 98 | 6 |
| 7.364 97 | 6 | |
| O | 0.068 15 | 6 |
| | 0.340 77 | 8 |
| | 0.681 55 | 12 |
| | 1.281 61 | 20 |
| | 2.101 40 | 26 |
| | 3.133 61 | 20 |
| | 4.198 91 | 12 |
| | 5.645 92 | 8 |
| 7.057 40 | 6 | |
| F | 0.065 30 | 6 |
| | 0.326 50 | 8 |
| | 0.653 00 | 12 |
| | 1.227 92 | 20 |
| | 2.013 37 | 26 |
| | 3.002 34 | 20 |
| | 4.023 01 | 12 |
| | 5.409 41 | 8 |
| 6.761 76 | 6 | |

TABLE II. Medium grid generation parameters.

| Atom | Radial shell position (bohr) | Points/Shell |
|-----------|------------------------------|--------------|
| H | 0.044 63 | 6 |
| | 0.223 17 | 8 |
| | 0.446 35 | 12 |
| | 0.845 46 | 20 |
| | 1.407 77 | 26 |
| | 2.179 98 | 20 |
| | 3.251 60 | 12 |
| | 4.064 50 | 8 |
| 5.080 63 | 6 | |
| Li | 0.142 94 | 6 |
| | 0.714 70 | 8 |
| | 1.429 41 | 12 |
| | 2.687 91 | 20 |
| | 4.407 27 | 26 |
| | 6.572 12 | 20 |
| | 8.806 37 | 12 |
| | 11.841 18 | 8 |
| 14.801 48 | 6 | |
| C | 0.071 12 | 6 |
| | 0.355 62 | 8 |
| | 0.711 25 | 12 |
| | 1.337 46 | 20 |
| | 2.192 98 | 12 |
| | 3.270 18 | 12 |
| | 5.000 00 | 6 |
| | 9.000 00 | 6 |
| N | 0.066 77 | 6 |
| | 0.333 87 | 8 |
| | 0.667 73 | 12 |
| | 1.255 63 | 20 |
| | 2.058 81 | 26 |
| | 3.070 10 | 20 |
| | 4.113 80 | 12 |
| | 5.531 48 | 8 |
| 6.914 35 | 6 | |
| O | 0.068 15 | 6 |
| | 0.340 77 | 8 |
| | 0.681 55 | 12 |
| | 1.281 61 | 20 |
| | 2.101 40 | 26 |
| | 3.133 61 | 20 |
| | 4.198 91 | 12 |
| | 5.645 92 | 8 |
| 7.057 40 | 6 | |
| F | 0.065 30 | 6 |
| | 0.326 50 | 8 |
| | 0.653 00 | 12 |
| | 1.227 92 | 20 |
| | 2.013 37 | 26 |
| | 3.002 34 | 20 |
| | 4.023 01 | 12 |
| | 5.409 41 | 8 |
| 6.761 76 | 6 | |

operator, as described in detail in Refs. 2, 3, and 5. The local least squares matrices for each atom are built from dealiasing sets that are typically a few hundred functions. Solution of the normal equations for such matrices is computationally trivial, and the overall effort scales linearly with molecule size as one simply adds an additional local operator for each new atom. For projection onto long range functions, the

length scales algorithm described earlier ensures that the dealiasing basis need only contain long range fitting functions, thus greatly reducing its size. This computational effort still formally grows as N^3 but has a very small prefactor for the molecules we examine here. For very large systems,

TABLE III. Fine grid generation parameters.

| Atom | Radial shell position (bohr) | Points/Shell | Atom | Radial shell position (bohr) | Points/Shell |
|-----------|------------------------------|--------------|------|------------------------------|--------------|
| H | 0.036 92 | 6 | N | 0.039 78 | 6 |
| | 0.184 62 | 8 | | 0.099 46 | 8 |
| | 0.369 24 | 12 | | 0.298 37 | 12 |
| | 0.742 67 | 26 | | 0.497 29 | 20 |
| | 1.229 44 | 50 | | 0.844 87 | 26 |
| | 1.854 85 | 50 | | 1.212 17 | 50 |
| | 2.645 36 | 26 | | 1.757 36 | 90 |
| | 3.516 97 | 12 | | 2.532 23 | 90 |
| | 4.496 08 | 8 | | 3.404 84 | 50 |
| | 5.620 10 | 6 | | 4.308 52 | 26 |
| Li | 0.070 09 | 6 | O | 0.040 61 | 6 |
| | 0.175 24 | 8 | | 0.101 52 | 8 |
| | 0.525 71 | 12 | | 0.304 55 | 12 |
| | 0.876 18 | 20 | | 0.507 58 | 20 |
| | 1.488 59 | 26 | | 0.862 35 | 26 |
| | 2.135 73 | 50 | | 1.237 25 | 50 |
| | 3.096 31 | 90 | | 1.793 72 | 90 |
| | 4.461 58 | 90 | | 2.584 62 | 90 |
| | 5.999 03 | 50 | | 3.475 29 | 50 |
| | 7.591 24 | 26 | | 4.397 66 | 26 |
| C | 10.034 18 | 20 | F | 5.812 88 | 20 |
| | 12.542 73 | 12 | | 7.266 10 | 12 |
| | 15.678 41 | 8 | | 9.082 62 | 8 |
| | 19.598 02 | 6 | | 11.353 28 | 6 |
| | 0.045 38 | 6 | | 0.038 91 | 6 |
| | 0.113 45 | 8 | | 0.097 26 | 8 |
| | 0.340 34 | 12 | | 0.291 79 | 12 |
| | 0.567 24 | 20 | | 0.486 31 | 20 |
| | 0.963 72 | 26 | | 0.826 23 | 26 |
| | 1.382 68 | 50 | | 1.185 41 | 50 |
| 2.004 56 | 90 | 1.718 57 | 90 | | |
| 2.888 44 | 90 | 2.476 35 | 90 | | |
| 3.883 80 | 50 | 3.329 70 | 50 | | |
| 4.914 60 | 26 | 4.213 44 | 26 | | |
| 6.496 17 | 20 | 5.569 37 | 20 | | |
| 8.120 21 | 12 | 6.961 71 | 12 | | |
| 10.150 27 | 8 | 8.702 14 | 8 | | |
| 12.687 83 | 6 | 10.877 67 | 6 | | |

straightforward strategies are available to reduce the scaling from N^3 to N (e.g., partitioning the molecule into regions).

Tables IV and V present the fitting basis (dealiasing set) associated with the grids described in Tables I, II, and III. Again, empirical optimization has been used to determine the exponents and angular momenta of each fitting function. Recall that in the local least squares method, fitting functions for projection onto a short range basis function are required only in the region where this function has substantial amplitude. Therefore, we define a fitting basis for each local least squares matrix in terms of functions on the "home" atom (i.e., the atom on which the function we are projecting onto is located), nearest neighbors, next nearest neighbors, etc., and this information is presented in Tables IV and V.

An important consequence of the new PS algorithms is that the results are much less sensitive to the fitting basis;

one can add a few extra functions without substantially affecting the results (significantly fewer fitting functions are required because the accuracy demanded in the PS part of the method is now significantly less). We therefore believe that the fitting basis in Tables IV and V is much more robust than those developed previously.

2. Two-electron integral correction control parameters

The most basic control parameters are those which determine which corrections scheme is used for each iteration and whether length scales is used. The correction schemes that are currently supported in PS-GVB are one-center corrections only for Coulomb or exchange, two- and three-center corrections as described for Coulomb and two-center correc-

TABLE V. Fine grid dealiasing functions. *Italics* indicate differences with the dealiasing functions used for the course and medium grid, as shown in Table IV.

| Atom | Exponent | | | | | | | | | | | | | |
|------|----------|----|--------|----|--------|----|--------|----|--------|----|--------|----|--------|----|
| | 0.0400 | | 0.0800 | | 0.1613 | | 0.3200 | | 0.6400 | | 1.1000 | | 2.2000 | |
| H | SR | LR | SR | LR | SR | LR | SR | LR | SR | LR | SR | LR | SR | LR |
| | 0 | 0 | 2 | 2 | 3 | 2 | 0 | 2 | 0 | 0 | 3 | 0 | 0 | 0 |
| | 0 | 0 | 2 | 0 | 3 | 0 | 2 | 0 | 2 | 0 | 3 | 0 | 0 | 0 |
| | 0 | 0 | 0 | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 2 | 0 | 0 | 0 |
| | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Li | 0.0100 | | 0.0180 | | 0.0360 | | 0.0800 | | 0.2000 | | 0.4000 | | 0.6000 | |
| | SR | LR | SR | LR | SR | LR | SR | LR | SR | LR | SR | LR | SR | LR |
| | 0 | 0 | 2 | 3 | 3 | 4 | 0 | 0 | 4 | 4 | 0 | 3 | 0 | 0 |
| | 0 | 0 | 0 | 0 | 2 | 0 | 0 | 0 | 2 | 0 | 0 | 0 | 0 | 0 |
| | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| C | 0.0400 | | 0.0840 | | 0.1687 | | 0.3500 | | 0.8000 | | 1.6000 | | 2.4000 | |
| | SR | LR | SR | LR | SR | LR | SR | LR | SR | LR | SR | LR | SR | LR |
| | 0 | 0 | 2 | 2 | 3 | 2 | 0 | 2 | 4 | 0 | 0 | 0 | 0 | 0 |
| | 0 | 0 | 2 | 0 | 3 | 0 | 3 | 0 | 4 | 0 | 0 | 0 | 0 | 0 |
| | 0 | 0 | 0 | 0 | 2 | 0 | 0 | 0 | 3 | 0 | 0 | 0 | 0 | 0 |
| | 0 | 0 | 0 | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| N | 0.0500 | | 0.1060 | | 0.2120 | | 0.4100 | | 0.8000 | | 1.6000 | | 2.4000 | |
| | SR | LR | SR | LR | SR | LR | SR | LR | SR | LR | SR | LR | SR | LR |
| | 0 | 0 | 2 | 2 | 3 | 2 | 0 | 2 | 4 | 0 | 0 | 0 | 0 | 0 |
| | 0 | 0 | 2 | 0 | 3 | 0 | 3 | 0 | 4 | 0 | 0 | 0 | 0 | 0 |
| | 0 | 0 | 0 | 0 | 2 | 0 | 0 | 0 | 3 | 0 | 0 | 0 | 0 | 0 |
| | 0 | 0 | 0 | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| O | 0.0700 | | 0.1350 | | 0.2700 | | 0.4800 | | 0.8000 | | 1.6000 | | 2.4000 | |
| | SR | LR | SR | LR | SR | LR | SR | LR | SR | LR | SR | LR | SR | LR |
| | 0 | 0 | 2 | 2 | 3 | 2 | 0 | 2 | 4 | 0 | 0 | 0 | 0 | 0 |
| | 0 | 0 | 2 | 0 | 3 | 0 | 3 | 0 | 4 | 0 | 0 | 0 | 0 | 0 |
| | 0 | 0 | 0 | 0 | 2 | 0 | 0 | 0 | 3 | 0 | 0 | 0 | 0 | 0 |
| | 0 | 0 | 0 | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| F | 0.0900 | | 0.1800 | | 0.3582 | | 0.5600 | | 0.8000 | | 1.6000 | | 2.4000 | |
| | SR | LR | SR | LR | SR | LR | SR | LR | SR | LR | SR | LR | SR | LR |
| | 0 | 0 | 2 | 2 | 3 | 2 | 0 | 2 | 4 | 0 | 0 | 0 | 0 | 0 |
| | 0 | 0 | 2 | 0 | 3 | 0 | 3 | 0 | 4 | 0 | 0 | 0 | 0 | 0 |
| | 0 | 0 | 0 | 0 | 2 | 0 | 0 | 0 | 3 | 0 | 0 | 0 | 0 | 0 |
| | 0 | 0 | 0 | 0 | 2 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |

TABLE VI. Default cutoff parameters.

| Iteration | 1 | 2 | 3 | 4 | 5 | 6 | 7+ |
|---|------------------|--------|--------|------------------|--------|--------|--------|
| Grid | Medium | Medium | Medium | Fine | Medium | Medium | Coarse |
| <i>F</i> matrix updating | No | Yes | Yes | No | Yes | Yes | Yes |
| 2- <i>e</i> ⁻ analytic corrections | Yes | No | No | Yes | No | No | No |
| Nonpolar function overlap cutoff | 10 ⁻² | | | 10 ⁻⁴ | | | |
| Polar function overlap cutoff | 10 ⁻¹ | | | 10 ⁻² | | | |
| Exchange inclusion distance cutoff | 3.0 | | | 5.0 | | | |
| Contraction pair prefactor cutoff | 10 ⁻⁸ | | | 10 ⁻⁸ | | | |
| Classical limit cutoff | 10 ⁻⁶ | | | 10 ⁻⁶ | | | |

will describe results for other basis sets, aside from preliminary *cc*-pVTZ basis set^{30,31} results we give in Sec. VI E. In general, the advantages of the PS method increase as the basis set becomes more dense (e.g., for a triple zeta basis) and when the shells in the basis set do not share exponents, as is the case in the present basis. Despite the fact that the present basis is the most advantageous DZP basis for standard two electron methods, we show here that significant timing improvements as compared to GAUSSIAN 92 can be obtained with minimal sacrifice of accuracy.

In previous work, we emphasized the agreement of absolute energies from PS-GVB and GAUSSIAN. However, insistence on such agreement for large molecules leads to loss of efficiency in PS-GVB. The only chemically relevant quantities are energy differences; indeed, it should be remembered that energies obtained by GAUSSIAN are themselves off by hundreds of kcal/mol from the exact differential equation solutions, due to basis set incompleteness. While absolute energy agreement is still in general very good (within a few tenths of a kcal/mol for the vast majority of cases), we have succeeded in developing grids, dealiasing sets, and iteration sequences in which the internal cancellation of error in PS-GVB is very reliable despite absolute energy differences with GAUSSIAN of as much as 1 kcal/mol for large molecules.

We have, in addition, developed parameter sets which do reliably reproduce the absolute energies from GAUSSIAN within 0.2 kcal/mol, even for quite large molecules where summation of the long range Coulomb fields to an accuracy of one part in 10^7 is very demanding. These parameter sets are $\sim 30\%$ slower than the default parameters; however, they allow the user to compare total energies directly with GAUSSIAN if this is desired. Discussion of such a tight parameter set, as well as the optimization of second-row atoms, is reserved for a subsequent paper.

It is important to realize that the issues addressed here with regard to the reliability of grid-based methods in electronic structure are just as crucial for density functional codes as they are for Hartree-Fock based wave function codes. To our knowledge, there have been no published papers in which the accuracy of relative energies for existing density functional codes (DGAUSS, DEMON, DMOL) has been examined for an extensive set of complicated molecules. Our experience is that some test cases are much more difficult to reproduce than others and that to conclude that the accuracy is adequate on the basis of tests on two or three simple molecules like ethane or benzene is grossly insufficient. Of course, one may not care about deviations of 0.1–1.0 kcal/mol in the energy, for example in the calculation of a metal-ligand bond energy of a few hundred kcal/mol where correlation errors will certainly be worse. However, for conformational energies of biological molecules, for example, or for evaluating the energy of different phases of a material, such errors can have significant chemical consequences and need to be understood.

B. Total energies

Table VII presents total energies for a wide range of molecules in their equilibrium geometries using GAUSSIAN 92 and the default and tight parameter sets for the 6-31G**

TABLE VII. Absolute energy comparisons: 6-31G** basis. Hartree-Fock energies (1 kcal/mol=0.0016 a.u.). GAUSSIAN 92: default cutoffs used.

| Molecule | <i>E</i> (G92) (hartrees) | <i>E</i> (PS) (hartrees) | ΔE (PS-G92) (kcal/mol) |
|--|------------------------------|-----------------------------|-----------------------------------|
| C ₂ H ₂ | -76.821 835 | -76.821 825 | 0.0063 |
| C ₆ H ₆ | -230.701 680 | -230.701 660 | 0.0125 |
| C ₂ H ₄ S | -475.525 899 | -475.525 982 | -0.0521 |
| C ₃ S ₂ H ₄ | -910.814 150 | -910.814 115 | 0.0220 |
| C ₄ H ₄ | -153.634 912 | -153.634 860 | 0.0326 |
| CH ₂ PH | -380.209 898 | -380.209 865 | 0.0207 |
| CH ₃ Cl | -499.088 628 | -499.088 617 | 0.0069 |
| CH ₃ SH | -437.664 129 | -437.664 034 | 0.0596 |
| CH ₃ SiH ₃ | -330.279 077 | -330.279 204 | -0.0797 |
| CH ₂ NH | -94.035 705 | -94.035 658 | 0.0295 |
| CH ₃ F | -139.038 781 | -139.038 719 | 0.0389 |
| CH ₃ CH ₂ OH | -154.089 013 | -154.088 985 | 0.0176 |
| H ₂ CO | -113.869 736 | -113.869 687 | 0.0307 |
| Glycylglycine | -489.550 210 | -489.549 941 | 0.1688 |
| Glutamine | -528.646 741 | -528.646 595 | 0.0916 |
| Glycine 0° | -282.844 462 | -282.844 579 | -0.0734 |
| H ₂ O ₂ | -150.770 782 | -150.770 599 | 0.1148 |
| H ₃ ⁺ | -1.293 591 | -1.293 587 | 0.0025 |
| HCN | -92.865 967 | -92.865 995 | -0.0176 |
| H ₂ CS | -436.469 855 | -436.469 858 | -0.0019 |
| H ₂ S ₂ | -796.177 451 | -796.177 420 | 0.0195 |
| H ₃ SiCl | -750.181 166 | -750.181 154 | 0.0075 |
| HCP | -379.106 572 | -379.106 702 | -0.0816 |
| HOCl | -534.847 156 | -534.847 147 | 0.0056 |
| HOCN | -167.729 020 | -167.729 334 | -0.1970 |
| CH ₃ OH | -115.045 719 | -115.045 630 | 0.0558 |
| CH ₄ | -40.201 399 | -40.201 470 | -0.0445 |
| NH ₂ CHO | -168.937 654 | -168.937 572 | 0.0515 |
| NH ₂ F | -154.959 172 | -154.959 114 | 0.0364 |
| Porphine | -983.163 305 | -983.163 186 | 0.0747 |
| P ₂ H ₄ | -683.756 972 | -683.757 103 | -0.0822 |
| S ₃ | -1192.441 335 | -1192.441 380 | -0.0282 |
| SC ₄ H ₄ | -550.917 166 | -550.917 146 | 0.0125 |
| Si ₂ H ₆ | -581.311 568 | -581.311 723 | -0.0973 |
| Si ₃ | -866.607 046 | -866.607 057 | -0.0069 |
| Si ₅ | -1444.431 461 | -1444.431 561 | -0.0627 |
| Si ₆ | -1733.362 994 | -1733.362 841 | 0.0960 |
| SiF ₂ | -487.862 531 | -487.862 486 | 0.0282 |
| SiH ₂ | -290.002 560 | -290.002 566 | -0.0038 |
| SiH ₃ F | -390.145 882 | -390.145 858 | 0.0151 |
| SiH ₄ | -291.230 804 | -291.230 822 | -0.0113 |
| SO ₃ | -621.980 612 | -621.980 732 | -0.0753 |
| Tyrosine | -626.232 318 | -626.232 230 | 0.0552 |
| Uracil | -412.479 477 | -412.479 089 | 0.2435 |
| H ₂ O | -76.023 615 | -76.023 596 | 0.0119 |

basis. For the cases shown here, the parameter set described above gives total energies that are very close to the GAUSSIAN results. These results are obtained with grids that are considerably smaller than those used in other numerical methods in electronic structure theory (~ 100 points/atom on most iterations as compared with ~ 1000 points/atom in typical density functional codes to obtain an accuracy that is significantly worse than what we report here). The improved performance is obtained by the use of pseudospectral methods, two-electron integral corrections, and length scales algorithms, as described earlier. The cost of the correction and length scales procedures is at present $\sim 30\%$ for the CPU time for a large molecule; the pseudospectral fitting proce-

TABLE VIII. Relative energy comparisons: 6-31G** basis. Hartree-Fock energies (1 kcal/mol=0.0016 a.u.).

| Molecule | E (G92) (hartree) | ΔE^a (kcal/mol) | E (PS) (hartree) | $\Delta\Delta E^b$ (kcal/mol) |
|-----------------------|------------------------|----------------------------|-----------------------|----------------------------------|
| glycine 0° | -282.844 462 | | -282.844 579 | |
| glycine 150° | -282.841 392 | 1.926 | -282.841 434 | 0.047 |
| glycine 180° | -282.841 665 | 1.755 | -282.841 680 | 0.064 |
| biphenyl 0° | -460.266 416 | | -460.266 008 | |
| biphenyl 22.5° | -460.268 991 | -1.616 | -460.268 656 | 0.045 |
| biphenyl 45.0° | -460.270 672 | -2.670 | -460.270 335 | -0.045 |
| biphenyl 67.5° | -460.269 115 | -1.693 | -460.268 682 | -0.015 |
| biphenyl 90.0° | -460.267 927 | -0.948 | -460.267 480 | -0.024 |
| diphenylether 30°-30° | -535.105 210 | | -535.104 526 | |
| diphenylether 40°-40° | -535.111 927 | -4.216 | -535.111 174 | -0.045 |
| diphenylether 50°-50° | -535.113 118 | -4.962 | -535.112 326 | -0.068 |
| diphenylether 60°-60° | -535.112 484 | -4.564 | -535.111 768 | -0.020 |
| diphenylether 70°-70° | -535.111 329 | -3.839 | -535.110 672 | 0.017 |
| diphenylether 80°-80° | -535.110 248 | -3.161 | -535.109 641 | 0.048 |
| diphenylether 90°-90° | -535.109 773 | -2.863 | -535.109 104 | 0.009 |

^aGAUSSIAN 92 energy differences calculated relative to the top listed energy for each method; the 0° conformers of glycine and biphenyl; the 30°-30° conformer of diphenyl ether.

^bPS-GVB energy differences show deviation from corresponding GAUSSIAN difference.

ture itself requires only the preprocessing time, which scales linearly with system size and is ~10% of the CPU time for porphine. From this analysis, we conclude that the techniques described here are considerably more efficient for a given level of accuracy than any published alternatives.

C. Relative energies

Table VIII compares energy differences for a selected set of molecular torsional barriers and conformations for GAUSSIAN 92 and PS-GVB for our parameter set, again using the 6-31G** basis. In all cases, the relative energies agree to better than 0.1 kcal/mol, independent of the size of the molecule. This demonstrates that PS-GVB now has its own cancellation of error comparable to that in GAUSSIAN 92. Again, we emphasize that the GAUSSIAN 92 results are nowhere near the Hartree-Fock limit due to basis set incompleteness, so that energy differences are in fact the only basis for a fair comparison of the two methods.

We have recently begun to study torsional energies as a function of electron correlation. Correlation effects can be on the order of several kcal/mol even for systems as simple as butane or urea. Consequently, the "errors" in PS-GVB energy differences are trivial compared to uncertainties due to basis

set and correlation effects. This argument applies even more strongly to bond energies where correlation effects are still larger. In summary, then, the performance of PS-GVB with regard to accuracy is quite adequate at the level of our parameter set optimized for computational efficiency and timing comparisons with GAUSSIAN at this level are meaningful.

D. Timing results: 6-31G** basis

Table IX presents CPU times for a selected set of molecules as compared to GAUSSIAN 92. For small molecules, a factor of 2 is obtained routinely for 6-31G** while for larger molecules a factor between 3-4 is obtained for both a Cray vector supercomputer and for an IBM Model 580 RISC workstation. These results do not represent a major breakthrough but they do reflect a significant quantitative advantage for the PS method. For other basis sets, the advantages are greater; the larger and more complex the basis set, the more the advantage of PS grows, as stated above. To illustrate this, we present results for the Dunning correlation-consistent TZP basis below.

TABLE IX. User CPU time comparisons: 6-31G** basis. All times in user CPU seconds.

| Molecule | Number of Basis Fcns | Workstation ^a | | Supercomputer | |
|------------|-------------------------|--------------------------|---------|---------------|---------|
| | | G92 time | PS time | G92 time | PS time |
| Water | 25 | 6.3 | 13.7 | 4.35 | 5.00 |
| Glycine 0° | 100 | 187.1 | 172.9 | 40.88 | 24.91 |
| Uracil | 140 | 542.3 | 340.9 | 76.42 | 36.93 |
| Glutamine | 200 | 1400.5 | 770.6 | 186.55 | 68.84 |
| Tyrosine | 250 | 2674.5 | 1207.8 | 311.02 | 104.90 |
| Porphine | 430 | 9941.0 | 3683.9 | 948.25 | 275.82 |

^aWorkstation is an IBM RS/6000 Model 580. Supercomputer is a Cray Y-MP C90. All calculations utilize direct SCF methods with symmetry explicitly turned off. Default cutoffs used in GAUSSIAN 92.

TABLE X. User CPU time comparisons: cc-pVTZ basis. All times are user CPU seconds.

| Molecule | Number of Basis Fcns | Supercomputer ^a | | ΔE (kcal/mol) |
|-----------------------|----------------------|----------------------------|-----------|-----------------------|
| | | G92 time | PS time | |
| Glycine 0° | 170 | 270.3196 | 160.3925 | -0.0471 |
| Uracil | 236 | 728.8067 | 272.9761 | 0.0477 |
| Glutamine | 340 | 2201.4424 | 533.4242 | -0.1004 |
| Diphenylether 30°-30° | 415 | 3615.1448 | 734.0660 | 0.0201 |
| Tyrosine | 424 | 4322.0474 | 809.7973 | -0.0998 |
| Porphine | 726 | 15 131.2271 | 2428.6439 | 0.1161 |

^aSupercomputer is a Cray Y-MP C90. All calculations utilize direct SCF methods with symmetry explicitly turned off. Default cutoffs used in all cases.

E. Timing results: cc-pVTZ basis

In Table X we show our preliminary cc-pVTZ (Refs. 30 and 31) results for a subset of molecules presented earlier; the larger molecules were chosen to better illustrate the scaling advantage of the PS method. Up to a factor of 6.5 improvement over GAUSSIAN 92 run with its default cutoffs is achieved in this size regime, showing the PS method's better scaling with basis set size. It should be noted that this basis set uses general contractions, which forces GAUSSIAN 92 to recalculate elementary integrals. However, PS-GVB must also recalculate these quantities and, therefore, this timing comparison is more directly illustrative than those for basis sets with shared exponents, such as 6-31G**, where as yet PS-GVB does not take advantage of this construct in its analytical two-electron package described earlier. With the expectation that future research will focus on larger molecules, as well as bigger basis sets to better model chemical properties, the utility of such a better scaling algorithm as the PS method in *ab initio* chemistry is apparent.

VII. CONCLUSION

We have demonstrated that PS methods are capable of reliable computing energy differences and total energies for the Hartree-Fock equations while displaying substantial acceleration of CPU time as compared to GAUSSIAN 92, which is generally accepted as the standard in the field; for single point Hartree-Fock direct self-consistent field calculations on large molecules without symmetry, we believe that GAUSSIAN 92 is the most efficient electronic structure code available using conventional analytical two electron integral methodology. A graphical user interface for UNIX systems has been constructed which makes PS-GVB easy to use as well. A description of the entire software package (as opposed to the present paper which has focused primarily upon algorithmic issues) will be presented elsewhere.

We have implemented an analytical gradient GVB correlation methods of various types, and a continuum treatment

of solvation based on accurate solution of the Poisson-Boltzmann equations using a new version of the DELPHI program.^{32,33} These results will be described in other publications. Density functional and localized MP2 algorithms are currently under development and we expect that very substantial savings in CPU times will be obtained in both cases as compared to existing methodology.

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