Advanced software for the calculation of thermochemistry, kinetics, and dynamics

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Abstract. The Born-Oppenheimer separation of the Schrödinger equation allows the electronic and nuclear motions to be solved in three steps: (1) the solution of the electronic wave function at a discrete set of molecular conformations; (2) the fitting of this discrete set of energy values in order to construct an analytical approximation to the potential energy surface (PES) at all molecular conformations; and (3) the use of this analytical PES to solve for the nuclear motion by using either time-dependent or time-independent formulations to compute molecular energy values, chemical reaction rates, and cumulative reaction probabilities. This project involves the development of technology to address all three of these steps. This report focuses on our recent work with nonlinear parameterization of the electronic wave functions.

1. Introduction

Our work this past year has focused on the use of nonlinear wave function parameters for electronic wave functions, on the computation of spin densities, and on the extension of our nonlinear wave function expansion approach to include spin-orbit interaction.

We have recently proposed a new expansion form for molecular electronic wave functions [1-6]. The wave function is written as a linear combination of graphically contracted functions (GCF), and each GCF in turn is formally equivalent to a linear combination of configuration state functions (CSFs) that comprise the underlying linear expansion space of dimension $N_{	ext{csf}}$. The CSF coefficients that define the basis functions are nonlinear functions of a smaller number of variables $N_{\phi}=N_{\text{csf}}$. This new approach addresses directly the main bottlenecks of previous electronic structure methods. Much of the computational effort and data storage requirements with this new approach depend only on $\log(N_{\text{csf}})$ rather than $N_{\text{csf}}$. The method is formulated in terms of spin-eigenfunctions using the Graphical Unitary Group Approach (GUGA)[7], and consequently it does not suffer from the spin contamination or spin instability that is often associated with single-reference electronic structure methods. The expansion form is appropriate for both ground and excited states and to closed- and open-shell molecules. The method is not based on the idea of expansion about a “reference” wave function, so its accuracy is not inherently limited because of failures of the Hartree-Fock method or artificially imposed excitation-level restrictions. The exact electronic Hamiltonian operator is used in this method; for example, it does not rely on multipole approximations or exchange-correlation operator approximations (although such approximations may prove useful within an optimization context as preconditioners). Our initial applications to some small molecules are encouraging. As demonstrated previously [4], even a single GCF, $N_{\phi}=1$, based on a $6^2$ Shavitt graph is sufficient to
dissociate the N≡N triple bond correctly to ground state $^4S$ atom fragments, two GCFs are sufficient to approach the full-valence CI electronic energy to within $3 \, mE_h$ at all bond lengths, and three GCFs reproduce exactly the full-valence CI energy at all bond lengths. More recently, we have demonstrated [5] convergence of the total energy to within 1 kcal/mole of the full-CI limit (the solution within the full tensor-product basis) with only 13 expansion terms, and to within $1 \, mE_h$ of the full-CI limit with only 16 expansion terms, at all bond lengths along the symmetric dissociation curve of H$_2$O to its atomic fragments O(P)+2H($^2S$).

2. Wave function optimization

Although the results described in the previous section are encouraging, the most remarkable feature of our new method is the relatively small effort required to construct hamiltonian matrix elements and transition density matrices in the GCF basis[2,3]. Given a wave function expansion of the form

$$|\psi\rangle = \sum_{\alpha} c_{\alpha} |P\rangle$$

in which the $N_{\alpha}$ GCFs are denoted $|P\rangle$, each basis function $|P\rangle$ depends on a corresponding set of nonlinear parameters $\varphi^P$ which in turn depend on the set of arc factors $\alpha^P$ associated with the arcs of the Shavitt graph. The wave function thereby depends on the linear expansion coefficients $c$ and on the nonlinear parameters $\varphi$. Optimization of the expansion coefficients $c$ to minimize the energy results in the symmetric generalized eigenvalue equation

$$H \, c = S \, c \, E$$

with $H_{pq} = \langle P | H | Q \rangle$ and $S_{pq} = \langle P | Q \rangle$. An efficient procedure has been developed to compute Hamiltonian matrix elements and reduced one- and two-particle density matrices for this nonlinear expansion form [2]. The effort required to construct an individual Hamiltonian matrix element $H_{pq}$ scales as $O(\beta n^4)$ for a wave function expanded in $n$ molecular orbitals. The prefactor $\beta$ itself scales between $N^0$ and $N^2$, for $N$ electrons, depending on the complexity of the underlying Shavitt graph. The corresponding metric matrix element $S_{pq}$ requires effort that scales as $O(\beta n)$. There is no component of the effort or storage for matrix element computation that scales as $N_{\alpha}$, which may be, practically speaking, arbitrarily large. Hamiltonian matrix element timings with our initial implementation of this method are very promising. Wave function expansions that are orders of magnitude larger than can be treated with traditional CI methods require only modest effort with our new method. A matrix element involving GCFs with $n=N=46$ corresponding to an underlying linear expansion space dimension $N_{\alpha}=5.5 \times 10^{24}$, or over 9.2 moles of CSFs, requires only a few seconds with our new method [2-4]. The computation of that same Hamiltonian matrix element using traditional full-CI technology is estimated to require about $10^8$ seconds, over a million times the age of the universe. Of course, a traditional full-CI code has the capability of computing $H_{pq}=x^P H x^Q$ for arbitrary vectors $x^P$ and $x^Q$, whereas our new method is restricted to vectors that can be represented in our graphical-based nonlinear expansion form. This restriction affects eventually $N_{\alpha}$, the number of GCFs required for convergence to chemical accuracy. These timings show the tremendous potential of our new method. $H_{pq}$ computation scales approximately the same as the simple Hartree-Fock method, yet the method is capable of approaching the accuracy of full-CI wave functions.

A major challenge presented by the new method is the optimization of the nonlinear parameters. In our previously published algorithm [3], each gradient evaluation requires $O(\beta n^3)$ effort, which is significantly more expensive than an energy evaluation, particularly for larger values of $n$. Typically, we find that our previous analytic gradient computation is 10 to 100 times faster than a finite difference approximation, and it is 10 to 100 times slower than a single energy computation. In last year’s proceedings [8], an example was given of the number of gradient evaluations that are required using various nonlinear optimization methods. For the conjugate-gradient and quasi-newton methods, hundreds or sometimes thousands of iterations might be required, each of which requires an expensive gradient evaluation. These methods along with the substitution and split-optimization methods are
based on the construction of the matrices \( G^{[u]} \) and \( S^{[u]} \), which are representations of the Hamiltonian and overlap matrices defined in a basis in which the GCFs are uncontracted at a particular orbital level \( u \). These matrices give a faithful representation of the energy in terms of the arc factors at a single orbital level \( \alpha^{[u]} \) within the assumption that the arc factors at all other levels are temporarily held fixed.

\[
E(\alpha^{[u]}) = \frac{\alpha^{[u]} G^{[u]} \alpha^{[u]}}{\alpha^{[u]} S^{[u]} \alpha^{[u]}}
\]

From this expression the analytic gradient and various optimization approaches follow. With our previous algorithm \([3,5]\), as each of the \( O(n^4) \) Shavitt-loop types is terminated, resulting in the contributions to \( H_{PQ} \) associated with a particular one- or two-electron contribution to the Hamiltonian, an immediate reverse (downward) propagation was performed, allowing the contributions to the separate \( G^{[u]} \) matrix elements to be accumulated. Each reverse propagation requires \( O(\beta n^3) \) computational effort, resulting in \( O(\beta n^5) \) total effort for all of the \( G^{[u]} \) matrices.

We have recently developed \([9]\) a new algorithm based on deferred reverse propagation. This algorithm may be understood by examining a particular sequence of Hamiltonian contributions. For simplicity, consider the one-electron contributions \( h_{pq} \) for \( p=1 \) and \( q=2,3,4 \) using the vector and sparse matrix notation introduced in \([2]\).

\[
H_{PQ} \leftarrow h_{12} \gamma_{(1)}^{PQ} F_{PQ}^{(1)} (R) F_{PQ}^{(2)} (R) \bar{\gamma}_{(2)}^{PQ} + h_{13} \gamma_{(1)}^{PQ} F_{PQ}^{(1)} (R) F_{PQ}^{(3)} (R) \bar{\gamma}_{(3)}^{PQ} + h_{14} \gamma_{(1)}^{PQ} F_{PQ}^{(1)} (R) F_{PQ}^{(4)} (R) \bar{\gamma}_{(4)}^{PQ}
\]

In these expressions \( \gamma_{(u)}^{PQ} \) is a row vector, \( F_{(u)}^{PQ}(W) \) are rectangular matrices (treated as a sparse data structure) of segment factors,

\[
F_{PQ}^{(u)}(W)_{\mu \nu} = \alpha_{\mu}^{(u)} \alpha_{\nu}^{(u)} T_{PQ}^{(u)}(W)_{\mu \nu}
\]

and \( \bar{\gamma}_{(u)}^{PQ} \) is a column vector. \( T_{PQ}^{(u)}(W)_{\mu \nu} \) is the Shavitt segment value of the appropriate shape \( W \) at orbital level \( u \). Our recursive \( H_{PQ} \) algorithm consists of extracting the common factors in each of these terms in left-to-right order.

\[
H_{PQ} \leftarrow h_{12} z_{(1)} (R) F_{PQ}^{(2)} (R) \bar{\gamma}_{(2)}^{PQ} + h_{13} z_{(2)} (R) F_{PQ}^{(3)} (R) \bar{\gamma}_{(3)}^{PQ} + h_{14} z_{(3)} (R) F_{PQ}^{(4)} (R) \bar{\gamma}_{(4)}^{PQ}
\]

with the row vectors \( z_{(u)} \) defined with a simple multiplicative recursion as follows.

\[
z_{(1)} = \gamma_{(1)}^{PQ} F_{PQ}^{(1)} (R)
\]

\[
z_{(k)} = z_{(k-1)} F_{PQ}^{(k)} (R) ; k = 2 \ldots (n-1)
\]

In general, this recursive algorithm requires \( O(\beta n^2) \) effort for all \( h_{pq} \) contributions for a given GCF pair \( PQ \). The construction of the \( G^{[1]} \) matrix with our previous algorithm would consist of three separate contributions from the right-to-left reverse propagation of the above three matrix expressions, or in general \( O(\beta n^3) \) effort for \( n \) orbitals for a \( PQ \) pair. Our new algorithm consists of accumulating these separate contributions recursively according to

\[
\bar{z}_{(4)} = h_{12} F_{PQ}^{(4)} (R) \bar{\gamma}_{(4)}^{PQ}
\]

\[
\bar{z}_{(k)} = h_{ik} F_{PQ}^{(k)} (R) \bar{\gamma}_{(k)}^{PQ} + F_{PQ}^{(k)} (R) z_{(k+1)} ; k = (n-1) \ldots 2
\]

giving (in principle)

\[
H_{PQ} \leftarrow \gamma_{(1)}^{PQ} F_{PQ}^{(1)} (R) \bar{z}_{(2)}
\]

from which the \( G^{[1]} \) contributions may be extracted in the single step

\[
C_{PQ}^{[1]} \leftarrow \gamma_{(1)}^{PQ} T_{(1)}^{PQ} (R) \bar{z}_{(2)}
\]

over all nonzero Shavitt segment values. This single step replaces the \( n \) separate accumulation steps of our previous algorithm. The total effort then requires only \( O(\beta n^2) \) for all \( h_{pq} \) contributions, reduced
from the $O(\beta n^3)$ effort of the previous algorithm. This deferred reverse propagation algorithm may be extended to the two-electron repulsion contributions to the Hamiltonian operator in a straightforward manner, and the $O(\beta n^3)$ effort of our previous algorithm is reduced to only $O(\beta n^4)$.

At the time of writing of this report, we have only partially implemented this algorithm. We hope to have this algorithm completely implemented and to present timing comparisons of both approaches by the time of the SciDAC meeting. A complete description of this new algorithm will be published separately [9]. However, it is clear even at this time that the new algorithm will be a significant improvement over our previous implementation, and it will allow new optimization algorithms to be considered that were impractical previously because of the relatively high costs of the $G^{[n]}$ matrix constructions. We expect our new algorithm to allow calculations on much larger molecular systems that are associated with larger values of $n$.

3. Spin-density computation

The GUGA formulation on which our nonlinear wave function expansion method is based is well-suited to the computation of spin-independent properties, including the electronic energy with no external magnetic field as discussed above. However, this approach complicates somewhat the computation of spin-dependent properties (those that depend on the magnetic quantum number $M$). In particular, the expectation value of such an operator may be written as

$$\langle \Psi; S, M | \hat{A} | \Psi; S, M \rangle = \sum_{p,q} A^{(1,0)}_{pq} D^{(1,0; M)}_{qp} = Tr \left( A^{(1,0)}_{pq} D^{(1,0; M)}_{qp} \right)$$

with the spin-density matrix defined in terms of the spin-orbital creation and annihilation operators as

$$D^{(1,0; M)}_{qp} = \langle \Psi; S, M | a^\dagger_{pq} a_{qp} - a^\dagger_{qp} a_{pq} | \Psi; S, M \rangle.$$  

It may be shown that this density matrix is related to the maximal $M=S$ spin-density matrix as

$$D^{(1,0; M)}_{\frac{M}{S}} = \frac{M}{S} D^{(1,0; S)}; M = -S, -S+1, \ldots, S-1, S$$

and that the maximal spin density matrix is given by

$$(S + 1) D^{(1,0; S)}_{\text{max}} = \left( 2 - \frac{1}{N} \right) D^{(0)}_{\text{max}} - \sum_k d_{\text{skip}}$$

with $D^{(0)}_{\text{max}} = \langle \Psi | \hat{E}_{pq} | \Psi \rangle$ and $d_{\text{skip}} = \langle \Psi | \hat{E}_{\text{skip}} | \Psi \rangle$, which in turn are both independent of $M$ and may be computed in a straightforward manner. The computation of the full set of $d_{\text{skip}}$ elements requires $O(\beta n^4)$ computational effort with a GCF wave function expansion. However, it is not the individual $d_{\text{skip}}$ elements that are required, but rather the particular summation over the orbital index $k$ indicated above. We have developed an algorithm to compute this summation recursively. Shavitt loop [2] types 4ab, 6ab, and 8ab, along with the two-level loop types 11ab, and 12ab, and the one-level loop type 14a must be included [10]. We demonstrate this recursive algorithm for the simple, but nontrivial, case of the Shavitt loop type 11b contributions which would normally require $O(\beta n^4)$ effort.

Consider the $q=4$ contributions for $k=1 \ldots 3$ for $d_{\text{skip}}$. With the matrix notation used in the previous section, the summation of the three contributions is as follows.

$$D^{(1,0; 3)}_{44} = \sum_k \gamma^{(3)}_{\text{skip}} \sum_k (RLF)^{\mu}_{(4)} (RLF)^{\mu}_{(3)} (RLF)^{\mu}_{(2)} (RLF)^{\mu}_{(1)}$$

$$+ \gamma^{(1)}_{\text{skip}} \sum_k (RLF)^{\mu}_{(4)} (RLF)^{\mu}_{(3)} (RLF)^{\mu}_{(2)} (RLF)^{\mu}_{(1)}$$

$$+ \gamma^{(2)}_{\text{skip}} \sum_k (RLF)^{\mu}_{(4)} (RLF)^{\mu}_{(3)} (RLF)^{\mu}_{(2)} (RLF)^{\mu}_{(1)}$$

The common factors in these terms may be computed using the recursive algorithm

$$z^{(0)}_{(1)} = \gamma^{(0)}_{\text{skip}} (RL)$$

$$z^{(0)}_{(2)} = \gamma^{(0)}_{\text{skip}} (RL) + z^{(0)}_{(k-1)} (RL) ; k = 2 \ldots (n - 1)$$

giving ultimately for an arbitrary $q$ contribution
This recursive procedure allows the row vectors $z^P_{(q)}$ to be computed with $O(\beta n)$ effort for each GCF pair $P$ and $Q$. The same approach applies also to the 11a Shavitt loop type using the corresponding segment factor matrices in the recursion expressions. By using this recursive approach, all $O(\beta n^2)$ individual contributions from the two-index 11ab Shavitt loops to the diagonal elements of the spin-density may be computed with only $O(\beta n)$ total effort. This same kind of recursion may be applied also to the three-index Shavitt loops 4ab, 6ab, and 8ab. The $O(\beta n^3)$ individual operator contributions to the off-diagonal spin-density matrix elements may be computed with only $O(\beta n^2)$ total effort[10].

4. Conclusions
We have presented the latest developments for our recently developed nonlinear wave function expansion form. The energy-based optimization is formulated in terms of a specific kind of uncontraction of each of the graphically contracted basis functions. These orbital-level Hamiltonian matrices give an intuitive representation of the energy as a function of disjoint subsets of the arc factors, they provide for an efficient computation of gradients of the energy with respect to the arc factors, and they allow optimal arc factors to be determined in closed form for subspaces of the full variation problem. Our new analytic gradient and orbital-level Hamiltonian matrix construction algorithm scales approximately as $O(\beta n^4)$, in contrast to our previous algorithm which scaled approximately as $O(\beta n^5)$. This new approach will allow applications of our new method to larger molecular systems, and it will allow new optimization algorithms to be considered that were previously impractical. Energy and gradient computations with our new method require relatively little effort compared to other electronic structure methods. Timings for energy and arc factor gradient computations involving expansion spaces of over $10^{24}$ CSFs have been reported. We have begun to extend our nonlinear expansion method to include spin-orbit interactions and to include the computation of magnetic properties (e.g., NMR and ESR spectra simulation). An algorithm has been presented that allows the reduced spin-density matrix to be computed with only $O(\beta n^2)$ effort.

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