Antisymmetrized Geminal Powers with Larger Chemical Basis Sets

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In previous research, we tested the wave function format of a linear combination of several antisymmetrized geminal power states. A numerical problem in the geminal matrices was noted, which made the total energies of electronic systems with large numbers of electrons unstable. The underlying cause was found to be the large cancellation term in the geminal power series. We have obtained a new format to resolve this problem for the case of total energies and partly for the first-order derivatives within the antisymmetrized geminal power states. By using this new formalism, we have calculated the ground state energies for several electronic systems, including the usage of a larger chemical basis set. The results are, in some cases, very close to the exact result, especially for one-dimensional Hubbard systems. Our result for a water molecule with the Dunning Zeta basis set is better than the CISD energy and approaches the CCSD energy.

There are many fascinating physical phenomena in macroscopic compounds of transitional metallic elements like cuprate superconductors. These physical phenomena are also chemical and governed partly by quantum chemical mechanisms. To obtain the energy spectra of these chemical systems, we have used the configuration interaction method or the coupled cluster formalisms. These methods have polynomial scaling in computational cost versus system size, but attempts at obtaining systematically good results increased the cost index of the scalings.

There are many wave function theories designed to conquer the problems of past decades, including the density matrices renormalization group methods (DMRG). The algorithm of DMRG is one example of matrix product states. When there are one-dimensional structures inherent to the electronic system, DMRG provides very good results. When applying the DMRG format to real molecules, we must sometimes assume a one-dimensional order of the chemical sites of the systems, which becomes increasingly unnatural when we increase the system size.

For the case of electronic systems, we have the knowledge of quantum Monte Carlo algorithms (QMC). Some of these algorithms use Slater determinants, and in some cases are further extended to use the so-called pfaffian or the antisymmetrized geminal power states (AGP) with Jastrow factors (JAGP). The combination of geminal powers and Jastrow factors has already obtained a variety of results for chemical systems. The formalism of QMC is based on Walker sampling with the usage of probability; thus, in obtaining the expectation value of the energies, we use the statistical average.

When using electronic functions larger than a one-electron density, we sometimes use the second-order reduced density matrices. The energy formula of the density matrices is very trivial in comparison to DFT formalisms, but there are known problem such as the N-representability of the density matrices. There are many ways to use the special conditions of the density matrices to conquer these problems. There are also suggestions for usage of antisymmetrized geminal power states, which are an extension of Slater determinants and very close analogues to the well-known BCS states. These AGP states are used to obtain the potential surfaces of molecules.

We have previously introduced the wave function assumption of the linear combination of antisymmetrized geminal power states to correctly and compactly describe the structures of many electronic wave functions. We hoped this format would provide an established workplace to describe larger chemical and physical systems in the future with a polynomial cost and high precision results. When we use the linear combination of Slater determinants instead of AGPs we can, in some cases, obtain results comparable to the exact value. AGPs describe larger variational spaces than the Slater determinants, so they are likely to provide better results. There are also recently reported results for geminal powers, and some provide results for the geminal product case, while others provide results for the restricted Hamiltonian case.

On the practice of the geminal power states with the electronic systems, we found that a numerical instability arises due to the matrices power structure of the format. We found that the cause of the problem is the cancellation of high-power terms when we obtain the total energy formula. We introduce how we obtained the solution in the forthcoming section. Furthermore, we report on recent calculation results with several antisymmetrized geminal power states. The geminal matrices technique was used, and we successfully enlarged the area of the system sizes such that we could calculate with the geminal power states.

First, we present the basic expressions in our AGP-based formalism. Some parts of these expressions have appeared in ref. We give the expression of the wave function as

$$\Psi (x_1 \cdots x_N) = \sum_{i_1 \cdots i_N = 1}^{M} A_{i_1 \cdots i_N} \phi_{i_1} (x_1) \cdots \phi_{i_N} (x_N),$$  (1)
\[ A_{k_1 \cdots k_N} = \sum_{k=1}^{K} c_k \tilde{A}(\gamma^k_{i_1} \gamma^k_{i_2} \cdots \gamma^k_{i_{N-1}}) \]  

(2)

Here, \( \Psi \) is the total wave function of the system, \( \phi \) is the one-electron orbital that is set to the Gaussian basis set or the Hubbard site orbital in our calculations, \( \tilde{A} \) is the antisymmetrizer, \( N \) is the number of the electron, \( M \) is the number of the one-electron orbital or of the basis function, and \( K \) is the number of AGPs which appear in the wave function. The geminal \( \gamma \) is a skew-symmetric matrix and there are no other restrictions. The expression for the total energy with the AGP states of \( \gamma^x \) and \( \gamma^y \) is

\[
E = \left( \sum_{k_1 l_1 k_2 l_2} \frac{1}{2} \text{pf}(1 + Bt) \cdot H_{k_1 l_1 k_2 l_2} \right) |(\gamma^x(1 + B t)^{-1})_{k_2 l_2} t| + \left( \sum_{k_1 l_1 k_2 l_2} \text{pf}(1 + Bt) H_{k_1 l_1 k_2 l_2} \right) |(\gamma^x(1 + B t)^{-1})_{k_2 l_2} t| \]

\[
- \left( \frac{1}{2} B(1 + B t)^{-1} |_{j=2} \right)_{l_1 k_1} (B(1 + B t)^{-1})_{l_2 k_1} + \frac{1}{2} B(1 + B t)^{-1} |_{l_1 k_1} (B(1 + B t)^{-1})_{l_2 k_2} \]

\[
- \frac{1}{2} B(1 + B t)^{-1} |_{i_1 l_1} (\gamma^x(1 + B t)^{-1})_{k_2 k_1} \cdot t^2 \]

(3)

We also apply the eigendecomposition of matrix \( B \) in the energy expression. This idea was obtained from the description in ref. [17].

\[
E = \sum_{k_1 l_1 k_2 l_2} \frac{1}{2} H_{k_1 l_1 k_2 l_2} \cdot ((\gamma^x Q r q_1 Q_l)_{k_2 k_1} |_{t_1 t_2} ) + \sum_{k_1 l_1 k_2 l_2} H_{k_1 l_1 k_2 l_2} \]

\[
- \left( \frac{1}{2} (Q r M \times Q r M q_2 Q_l \times Q_l)_{l_1 k_2 l_2 k_1} \right) + \frac{1}{2} (Q r M \times Q r M q_2 Q_l \times Q_l)_{l_1 k_1 l_2 k_2} \]

\[
- \frac{1}{2} (Q r M \times \gamma^x Q r q_2 Q_l \times Q_l)_{l_1 l_2 k_1 k_2} \]

(7)

where

\[
q_{1 i_1 i_2} = \frac{\partial}{\partial \lambda_{i_1}} \text{pf}(1 + Bt) |_{t \in \mathbb{R}} \]

(8)

\[
q_{2 i_1 i_3 i_4} = \frac{\partial}{\partial \lambda_{i_1}} \frac{\partial}{\partial \lambda_{i_3}} \text{pf}(1 + Bt) |_{t \in \mathbb{R}} \]

(9)

Or, alternatively, we have

\[
q_{10 i_1 i_2} = (1 + Mt)_{l_1 l_2}^{-1} \text{pf}(1 + Bt) |_{l \in \mathbb{R}} \]

(10)

\[
q_{20 i_1 i_3 i_4} = (1 + Mt)^{-1} (1 + Mt)_{i_1 i_2}^{-1} \text{pf}(1 + Bt) |_{t \in \mathbb{R}} \]

(11)

The notations \( q_{10} \) and \( q_{20} \) are the original formalisms of the energies \( q_1 \) and \( q_2 \) are modified ones which are used instead of \( q_{10} \) and \( q_{20} \). For the above expressions, the set of indices \( i_1 i_2 \) or \( i_3 i_4 \) always appear as diagonal and the non-diagonal part is set to zero. This modification removes the inverse matrices even though they are given as matrix polynomials. The tensor given in [9] can be distributed as a two-dimensional plane in the four-dimensional space of indices and has the twofold structure of the usual diagonal matrices. The definition of the tensor algebra with the cross term is such that

\[
(A \times B q C \times D)_{i_1 i_2 i_3 i_4} = \sum_{k_1 k_2 k_3} A_{i_1 k_1} B_{i_2 k_2} q_{k_1 k_2 k_3} C_{k_2 k_3} D_{i_2 j_2} \]

(12)

Equations [8] and [10] give the same value. However, equations [9] and [11] are different in the sense that in [9], the \( i_1 = i_3 \) term is neglected. We numerically found that we could obtain the same value for the total energy with this modification in the energy expression. With this modification, we successfully reproduced the total energy of STO-3G water converged case. In this case, the energy was obtained with quadruple precision arrays in previous research [20], but we were able to reproduce
almost the same energy with the same input geminal matrices using double precision arrays. From this we have concluded that the stabilization of the total energy with double precision variables is achieved by use of this eigenvalue technique. We can further obtain the algorithm to partially stabilize the first-order derivative of the energy with respect to geminals in a similar manner.

We have applied the ESTD formalism on a water molecule and the Hubbard model using the stabilized form of ESTD described above. We have done the variational process with the quasi-Newton Broyden-Fletcher-Goldfarb-Shanno algorithm (BFGS) method. For the water molecule, we have tested the STO-3G basis set and the Dunning zeta (DZ) basis set. The geometry is set to O: (0,0,0,0,0), H: (−1.809,0,0,0,0), H: (0.453549,1.75221,0,0) for STO-3G and O: (0,0,0,0,0), H: (1.515263,0.0,−1.058898), H: (−1.515263,0.0,−1.058898) for DZ. For the STO-3G case, we have used the same system as that of ref.[26]. For the DZ basis case, we have used the system in ref.[2]. For the Hubbard model, we have used the one-dimensional Hubbard model with six sites. The parameter $U/t$ is set to 1.0 and 10.0.

| Method          | Total energy |
|-----------------|--------------|
| Hartree-Fock    | −74.962940033 |
| ESTD, $K = 1$   | −74.987449763 |
| ESTD, $K = 4$   | −75.011647636 |
| ESTD, $K = 8$   | −75.012339655 |
| ESTD, $K = 16$  | −75.012415900 |
| Exact (ours)    | −75.012425818 |
| Exact (Gaussian)| −75.012425839 |

**TABLE I: Total energy (in units of hartrees) of H$_2$O with STO-3G basis set obtained by ESTD. For comparison, the full-CI calculation with our own code and the CASSCF calculation using the Gaussian09 package was taken from ref.[2]. The Hartree-Fock calculation was done with our own code.**

Table I shows our results for the water molecule with STO-3G basis set. The ESTD energy starts between the Hartree-Fock (HF) and full-CI values. Then, the ESTD result rapidly approaches the exact value. In this system, $M = 14$, $N = 10$, and the total dimension of the Hilbert space is set to 1001. The residual energy is $1.0 \times 10^{-5}$ hartree when $K = 16$. In table I we have shown the results for the water molecule with the DZ basis set. In this system, $M = 28$, $N = 10$, and the total dimension of the Hilbert space is 13123110. When the spin and space adaptations were done correctly, the dimension became 2564732. If this was done with the ESTD algorithm, the numerical difficulty of searching for the correct ground state in the total Hilbert space would be dramatically reduced. In this system, the variation reaches the area beyond 95 percent of the total correlation energy. The ESTD energy of $K = 1$ is slightly below the Hartree-Fock energy, which could be an important sign that the variational space for one AGP state is larger than one Slater determinant. The Configuration Interaction (CISD) and Coupled Cluster (CCSD) values are also shown from the references. Our result of ESTD, $K = 60$ is better than the CISD energy. The result describes more than 98 percent of the correlation energy and closely approaches the CCSD energy. In this system, the residual energy is $2.8 \times 10^{-3}$ hartree when $K = 60$. The calculation of $K = 60$ is done under the condition that each AGP state that appears in eq.(2) has the same weight. In tables III and IV we have shown the results for the one-dimensional six-site Hubbard model with $U/t = 1.0$ and $U/t = 10.0$. For both systems, $M = 12$, $N = 6$, and the total dimension of the Hilbert space is set to 924. In both cases, the ESTD energy is well-converging to the exact value. For the system with $U = 1.0$, the residual energy is $3.9 \times 10^{-6}$ when $K = 16$. For the system with $U = 10.0$, the residual energy is $3.3 \times 10^{-6}$ when $K = 16$.

| Method          | Total energy |
|-----------------|--------------|
| Hartree-Fock    | −6.500000000 |
| ESTD, $K = 1$   | −6.534626699 |
| ESTD, $K = 4$   | −6.597850211 |
| ESTD, $K = 8$   | −6.601012609 |
| ESTD, $K = 16$  | −6.60154349  |
| Exact (ours)    | −6.60115829  |
| Exact (ref[19]) | −6.60115829  |

**TABLE II: Total energy (in units of hartrees) of H$_2$O with DZ basis set obtained by ESTD. For comparison, the full-CI calculation was taken from ref.[2]. The Hartree-Fock calculation was done with our own code and agrees with the value in ref.[2]. The CISD calculation in ref.[2] and the CCSD calculation in ref.[3] are also shown.**

| Method          | Total energy |
|-----------------|--------------|
| Hartree-Fock    | −76.009837600 |
| ESTD, $K = 1$   | −76.03854235 |
| ESTD, $K = 4$   | −76.13814833 |
| ESTD, $K = 8$   | −76.14419119 |
| ESTD, $K = 16$  | −76.14774318 |
| ESTD, $K = 40$  | −76.14917592 |
| ESTD, $K = 60$  | −76.15509884 |
| CISD (ref.[2])  | −76.1500151  |
| CCSD (ref.[3])  | −76.1560786  |
| Exact (ref[2])  | −76.157866   |

**TABLE III: Total energy of six site Hubbard model with $U/t=1.0$ obtained by ESTD. For comparison, the full-CI calculation with our own code and the result of ref.[14] is shown.**
| Method          | Total energy           |
|-----------------|------------------------|
| Hartree-Fock    | -1.18824301            |
| ESTD, $K = 1$   | -1.26387314            |
| ESTD, $K = 4$   | -1.51073560            |
| ESTD, $K = 8$   | -1.65861524            |
| ESTD, $K = 16$  | -1.66435948            |
| Exact (ours)    | -1.66436273            |
| Exact (ref.[19])| -1.66436273            |

TABLE IV: Total energy of six site Hubbard model with $U/t=10.0$ obtained by ESTD. For comparison, the full-CI calculation with our own code and the result of ref.[19] is shown. The Hartree-Fock calculation was done with our own code.

In Fig.1, we have plotted the behavior of relative energy with respect to exact value and the energy gradient with respect to the geminal variables. We have used the root mean square for the value of the geminal gradient. In each case, the value of the gradient is also decreasing as the variation progresses. These first-order derivatives are combined with the BFGS Hessian matrices and determine the direction of the variational search of the geminals.

We have observed that by the application of the eigenvalue technique with AGPs, the instability of the energy and some of the variational process is removed. We were therefore able to perform the ESTD calculations with double precision arrays and general skew-symmetric matrices without the usage of quadruple or higher arithmetic. As a result, the ESTD calculation of general matrices became dramatically faster than before. The energy error for the DZ basis case is around three millihartree in this case, which is comparable to the error in the Hilbert space JAGP case[12]. This energy error is likely to be further decreased when we increase the number of AGPs. For the case of the Hubbard models, the behavior of residual energies shows that the exponential convergence toward the exact solution is likely against
FIG. 4: The relative energy and the energy gradient on the variation of the one dimensional six site Hubbard model with \( U/t = 10.0 \). The number of AGPs (\( K \)) is set to 16.

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