

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 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 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 double zeta basis set is better than the configuration-interaction singles and doubles energy and approaches the coupled cluster singles and doubles energy.

DOI: [10.1103/PhysRevA.99.012519](https://doi.org/10.1103/PhysRevA.99.012519)**I. INTRODUCTION**

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 [1–3]. 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) [4,5]. 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 [6]. 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 [7].

For the case of electronic systems, we have successful results of quantum Monte Carlo algorithms (QMC) [8]. 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 [9–13]. 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 [14,15]. QMC algorithms on electronic systems are also known to suffer from the fermionic negative sign problem [8].

On the other hand, there are theories of the reduced density matrices of fermionic systems in order to mathematically clarify the nature of electronic correlations in many-body systems [16,17]. The energy formula for the density matrices

is very trivial in comparison to DFT formalisms, but there are known problem such as the N -representability conditions of the density matrices [18]. There are also algorithms to consider the necessary conditions of the density matrices in order to obtain the lowest energy of target systems [19]. In the context of reduced density matrices, there are suggestions for the wave-function form of antisymmetrized geminal power states, which are an extension of Slater determinants and very close analogs to the well-known BCS states [16,17,20–22]. These AGP states are used to obtain the potential surfaces of molecules [23,24].

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 [25,26]. 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 [27]. One AGP state describes larger variational space than one Slater determinant, so the linear combination of AGPs is likely to provide better results. There are also recently reported results for geminal powers, and some provide results for the geminal product case [28,29], while others provide results for the restricted Hamiltonian case [30].

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.

II. FORMALISM

First, we present the basic expressions in our AGP-based formalism. Some parts of these expressions have appeared in Ref. [26]. We give the expression of the wave function as

$$\Psi(x_1 \cdots x_N) = \sum_{i_1 \cdots i_N=1}^M A_{i_1 \cdots i_N} \phi_{i_1}(x_1) \cdots \phi_{i_N}(x_N), \quad (1)$$

$$A_{i_1 \cdots i_N} = \sum_{k=1}^K c_k \hat{A}(\gamma_{i_1 i_2}^k \gamma_{i_3 i_4}^k \cdots \gamma_{i_{N-1} i_N}^k). \quad (2)$$

Here, Ψ is the total wave function of the system, ϕ is the one-electron orbital that is set to the Gaussian basis set or the Hubbard site orbital in our calculations, \hat{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 γ is a skew-symmetric matrix and there are no other restrictions. The expression for the total energy with the AGP states of γ^x and γ^y is

$$E = \left[\sum_{k_1 l_1 k_2 l_2} \frac{1}{2} \text{pf}(1 + Bt) \cdot H_{k_1 l_1 k_2 l_2} \{[\gamma^x(1 + Bt)^{-1}]_{k_2 k_1} (\gamma^y)_{l_1 l_2}\} t + \sum_{k_1 l_1 k_2 l_2} \text{pf}(1 + Bt) H_{k_1 l_1 k_2 l_2} \right. \\ \times \left(-\frac{1}{2} [B(1 + Bt)^{-1}]_{l_1 k_2} [B(1 + Bt)^{-1}]_{l_2 k_1} + \frac{1}{2} [B(1 + Bt)^{-1}]_{l_1 k_1} [B(1 + Bt)^{-1}]_{l_2 k_2} \right. \\ \left. \left. - \frac{1}{2} [B(1 + Bt)^{-1} \gamma^y]_{l_1 l_2} [\gamma^x(1 + Bt)^{-1}]_{k_2 k_1} \right) \cdot t^2 \right] \Bigg|_{t^{N/2}}, \quad (3)$$

where H is the Hamiltonian matrix element and the matrix B is defined as

$$B = -\gamma^y \gamma^x. \quad (4)$$

These are the basic formalisms of extended symmetric tensor decomposition (ESTD). These expressions for the AGP states are somewhat similar in their structure to expressions found in nuclear physics, though they do not contain the polynomial expressions [31–34].

Next, we show how numerical stabilization of the energy is obtained. We diagonalize the matrix B as

$$B = Q_r M Q_l. \quad (5)$$

The matrix B is defined as a product of two skew-symmetric matrices and has a relationship with the so-called skew Hamiltonian matrices. Therefore, the eigenvalues of B are evenly degenerate. For such matrices, the details of the eigenvalue decompositions can be found in Refs. [35–37]. When the eigenvalues of B are $\lambda_1, \lambda_1, \dots, \lambda_{M/2}, \lambda_{M/2}$, we can rewrite the norm as

$$n = N! \text{pf}(1 + Bt)|_{t^{N/2}} = N! [\det(1 + Bt)]^{1/2}|_{t^{N/2}} = N! \sqrt{(1 + \lambda_1 t)^2 \cdots (1 + \lambda_{M/2} t)^2}|_{t^{N/2}} = N! [(1 + \lambda_1 t) \cdots (1 + \lambda_{M/2} t)]|_{t^{N/2}}. \quad (6)$$

We also apply the eigendecomposition of matrix B in the energy expression. This idea was obtained from the description in Ref. [17]:

$$E = \sum_{k_1 l_1 k_2 l_2} \frac{1}{2} H_{k_1 l_1 k_2 l_2} [(\gamma^x Q_r q1 Q_l)_{k_2 k_1} (\gamma^y)_{l_1 l_2}] + \sum_{k_1 l_1 k_2 l_2} H_{k_1 l_1 k_2 l_2} \left(-\frac{1}{2} (Q_r M \times Q_r M q2 Q_l \times Q_l)_{l_1 k_2 l_2 k_1} \right. \\ \left. + \frac{1}{2} (Q_r M \times Q_r M q2 Q_l \times Q_l)_{l_1 k_1 l_2 k_2} - \frac{1}{2} (Q_r M \times \gamma^x Q_r q2 Q_l \gamma^y \times Q_l)_{l_1 l_2 k_2 k_1} \right), \quad (7)$$

where

$$q1_{i_1 i_1} = \frac{\partial}{\partial \lambda_{i_1}} \text{pf}(1 + Bt)|_{t^{N/2-1}}, \quad (8)$$

$$q2_{i_1 i_3 i_1 i_3} = \frac{\partial}{\partial \lambda_{i_1}} \frac{\partial}{\partial \lambda_{i_3}} \text{pf}(1 + Bt)|_{t^{N/2-2}}. \quad (9)$$

Or, alternatively, we have

$$q10_{i_1 i_1} = (1 + Mt)_{i_1 i_1}^{-1} \text{pf}(1 + Bt)|_{t^{N/2-1}}, \quad (10)$$

$$q20_{i_1 i_3 i_1 i_3} = (1 + Mt)_{i_1 i_1}^{-1} (1 + Mt)_{i_3 i_3}^{-1} \text{pf}(1 + Bt)|_{t^{N/2-2}}. \quad (11)$$

The notations $q10$ and $q20$ are the original formalisms of the energies and $q1$ and $q2$ are modified ones which are used instead of $q10$ and $q20$. For the above expressions, the set of indices $i_1 i_1$ or $i_3 i_3$ always appear as diagonal and the nondiagonal 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

TABLE I. Total energy (in units of hartrees) of H₂O 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. [26]. The Hartree-Fock calculation was done with our own code.

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

term is such that

$$(A \times B q C \times D)_{i_1 j_1 i_2 j_2} \equiv \sum_{k_1 l_1 k_2 l_2} A_{i_1 k_1} B_{i_2 l_1} q_{k_1 l_1 k_2 l_2} C_{k_2 j_1} D_{l_2 j_2}. \quad (12)$$

Equations (8) and (10) give the same value. However, Eqs. (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 [26], 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.

TABLE II. Total energy (in units of hartrees) of H₂O 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	-76.00983760
ESTD, $K = 1$	-76.03854235
ESTD, $K = 4$	-76.13814833
ESTD, $K = 8$	-76.14419119
ESTD, $K = 16$	-76.14774318
ESTD, $K = 40$	-76.14971592
ESTD, $K = 60$	-76.15509884
CISD (Ref. [2])	-76.150015
CCSD (Ref. [3])	-76.156078
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. [19] is shown. The Hartree-Fock calculation was done with our own code.

Method	Total energy
Hartree-Fock	-6.50000000
ESTD, $K = 1$	-6.53462699
ESTD, $K = 4$	-6.59785021
ESTD, $K = 8$	-6.60101260
ESTD, $K = 16$	-6.60115439
Exact (ours)	-6.60115829
Exact (Ref. [19])	-6.60115829

III. RESULTS

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 double zeta (DZ) basis set. The geometry is set to O : (0.0, 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, -0.009), 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.

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 1.0×10^{-5} hartree when $K = 16$. In Table II, 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 256473 [2]. 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

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.

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

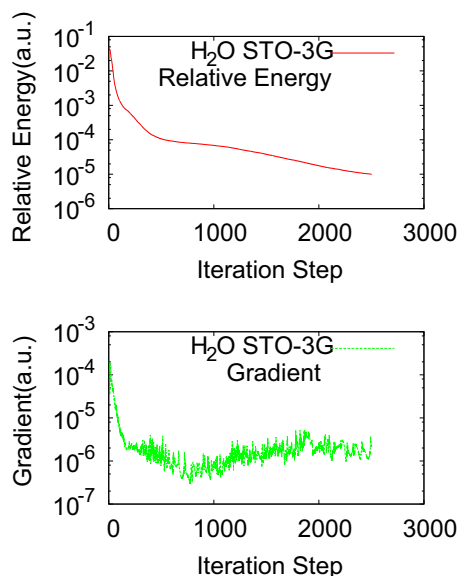


FIG. 1. Relative energy and the energy gradient on the variation of the water molecule with STO-3G basis set. The number of AGPs (K) is set to 16.

dramatically reduced. In this system, the variation reaches the area beyond 95% 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 singles and doubles (CISD) and coupled cluster Slater determinant (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% of the correlation energy and closely approaches the CCSD energy. In this system, the residual energy is 2.8×10^{-3} hartree when $K = 60$. The calculation of

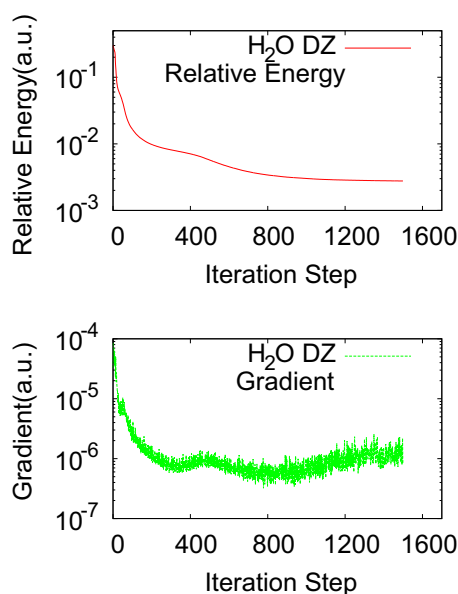


FIG. 2. Relative energy and the energy gradient on the variation of the water molecule with DZ basis set. The number of AGPs (K) is set to 60.

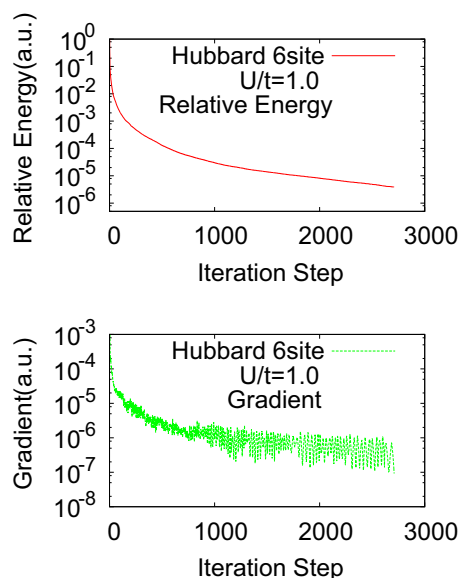


FIG. 3. Relative energy and the energy gradient on the variation of the one-dimensional six-site Hubbard model with $U/t = 1.0$. The number of AGPs (K) is set to 16.

$K = 60$ 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 3.9×10^{-6} when $K = 16$. For the system with $U = 10.0$, the residual energy is 3.3×10^{-6} when $K = 16$.

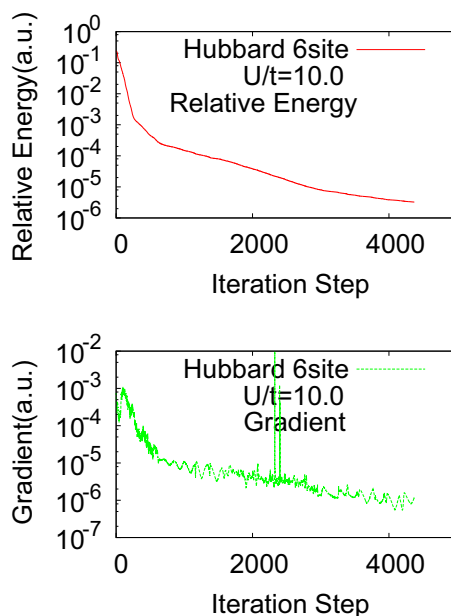


FIG. 4. Relative energy and the energy gradient on the variation of the one-dimensional six-site Hubbard model with $U/t = 10.0$. The number of AGPs (K) is set to 16.

In Figs. 1–4, 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.

IV. CONCLUSION

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 the number of terms in ESTD. We have not optimized our formalism for spin adaptations, but if that is done correctly, we expect overall improvement of the variation. Also, we could calculate the excited states within the ESTD formalism by using the orthogonality conditions of the quantum states. All calculations apart from the $K = 1$ case have been done with the parallelization for the K^2 part of the ESTD algorithm.

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