Evolutionary algorithm based configuration interaction approach

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A stochastic configuration interaction method based on evolutionary algorithm is designed as an affordable approximation to full configuration interaction (FCI). The algorithm comprises of initiation, propagation and termination steps, where the propagation step is performed with cloning, mutation and cross-over, taking inspiration from genetic algorithm. We have tested its accuracy in 1D Hubbard problem and a molecular system (symmetric bond breaking of water molecule). We have tested two different fitness functions based on energy of the determinants and the CI coefficients of determinants. We find that the absolute value of CI coefficients is a more suitable fitness function when combined with a fixed selection scheme.

Keywords: genetic algorithm, evolutionary algorithm, configuration interaction

Majority of the electronic structure methods that have been developed and used over the last few decades starts with the independent orbital approximation, i.e. the assumption that a single Slater determinant is a qualitatively correct starting point for a calculation. This qualitatively correct reference is typically corrected for dynamic correlation with post Hartree Fock (HF) methods such as Moller-Plesset perturbation theory (MP2) or coupled cluster singles and doubles (CCSD). However, the assumption of a single Slater determinant as a reference is not qualitatively correct, especially in situations where there are significant orbital degeneracies or near-degeneracies, e.g., bond breaking or di- and tri-radicals. Such systems are referred to as strongly correlated systems and the electronic correlation in these systems are referred to as static correlation, as opposed to dynamic correlation. It is important to note that we are not differentiating between true correlation due to orbital degeneracies and that required to treat proper spin symmetry (non-dynamic and static correlations)\textsuperscript{10,11}

Full configuration interaction (FCI) is the most rigorous method to treat correlation, both static and dynamic. However, FCI involves exact diagonalization of the full Hamiltonian in its Hilbert space and is therefore, not affordable for reasonable system sizes and basis sets\textsuperscript{4}. Therefore, approximate methods such as CASSCF\textsuperscript{5} and RASSCF\textsuperscript{6} etc have been developed where only a subset of the orbital space is treated exactly to reduce the computational cost. But these methods also involve an exact diagonalization, albeit over a smaller sub-space. On the other hand, density matrix renormalization group (DMRG)\textsuperscript{8,9} have been developed to circumvent the exact diagonalization problem and therefore, the associated exponential scaling. While DMRG has been remarkably successful in the case of pseudo-linear systems, more general 2D and 3D systems are complicated due to problems in orbital ordering\textsuperscript{8,9,12,13} However, there have been developments towards using tensor networks to alleviate this problem\textsuperscript{12,13} Antisymmetrized geminal power (AGP) wavefunctions have also been a powerful technique for strongly correlated systems\textsuperscript{14,15}

A completely different approach is taken by stochastic algorithms such as quantum Monte Carlo (QMC)\textsuperscript{16–19} The approach uses Monte Carlo or Metropolis algorithm to propagate the walkers into the important part of the Hilbert space. Several flavors of QMC have been developed, most notable of which is the FCI-QMC by Alavi and co-workers\textsuperscript{20} There have also been other stochastic approaches such as stochastic coupled cluster method\textsuperscript{21}

Evolutionary and genetic algorithm provides an alternative to these stochastic approaches. It has similarities to Monte Carlo Configuration Interaction (MCCI)\textsuperscript{22} and adaptive configuration interaction (ACI)\textsuperscript{23} methods. Depending on the judicial use of fitness function in the evolutionary algorithm and generation of new populations, it can lead to extremely fast convergence to the correct solution. In this work, we adapt genetic algorithm (GA) for its use in electronic structure problem. To probe the efficiency of the method, we have tested it for 2 systems - 1D Hubbard model and molecular system such as symmetric bond breaking in H$_2$O.

The fermionic wavefunction of any correlated system can be written as

$$|\Psi\rangle = \sum_i c_i |D_i\rangle,$$

where $|D_i\rangle$ is the $i^{th}$ Slater determinant,

$$|D_i\rangle = |D_{i_1, i_2, \ldots, i_N}\rangle = \frac{1}{\sqrt{N!}} \begin{bmatrix} \phi_{i_1}(1) & \phi_{i_2}(2) & \ldots & \phi_{i_1}(N) \\ \phi_{i_1}(1) & \phi_{i_2}(2) & \ldots & \phi_{i_2}(N) \\ \vdots & \vdots & \ddots & \vdots \\ \phi_{i_N}(1) & \phi_{i_N}(2) & \ldots & \phi_{i_N}(N) \end{bmatrix}$$

where the $\phi_{i_n}(m)$ denotes the occupation of electron $m$ in the orbital $i_n$. The Hilbert space grows exponentially and therefore, the exact solution for this FCI problem is possible for only small systems in small basis sets.

One can however, envisage solving this problem in a stochastic manner such that the important parts of the
FIG. 1. The schematics of the algorithm used is shown. It consists of the following steps: (i) Initiation; (ii) Expansion of basis by replication, mutation and crossover; (iii) Selection of the new population using the fitness function.

Hilbert space (i.e., Slater determinants with large coefficients $c_i$) are sampled in an intelligent manner. Metropolis algorithm or Monte Carlo is one such method for stochastic sampling of the Hilbert space. An alternative approach is to use evolutionary algorithms. In our genetic algorithm configuration interaction (GACI), the important steps are: (i) Initiation; (ii) Propagation by (a) cloning, (b) mutation and (c) cross-over; (iii) Evaluation of the fitness of the Slater determinant; and (iv) Selection, i.e., retaining the fittest Slater determinants for the next generation population. Using these four steps iteratively, the population of the Slater determinants are improved and the lowest energy population is retained as the variationally approximated wavefunction (schematics are given in Fig. 1). The details of each steps of the algorithm are:

**Initiation**: A GACI calculation is initiated by a random set of Slater determinants. In order to improve convergence the random set includes the determinant where the electrons (fermions) reside in the lowest energy orbitals. In case of the molecular Hamiltonian, this denotes the Hartree Fock wavefunction.

**Propagation**: To create new generations, Slater determinants are added to the old population (set of Slater determinants included in the previous iteration). This is done using three different approaches with specific probabilities. The probabilities can be tuned to achieve faster convergence. Pictorially, the different propagator operations are given in Fig. 2. (a) Mutation (b) Crossover

**Replication/Cloning** - The Slater determinants $|D_{i,old}\rangle$ in the previous iteration are always retained/copied in the new generation.

**Mutation** - The Slater determinants are mutated with a probability $p_1$. Mutation of a Slater determinant $|D_{i,old}\rangle$ is defined as the action of a CI singles operator $a_i^+a_j$ on $|D_{i,old}\rangle$,

$$|D_{i,new}^1\rangle = a_i^+a_j|D_{i,old}\rangle,$$

such that $i_j$ is an occupied orbital, and $i_k$ is an unoccupied orbital in the old Slater determinant.

**Crossover** - The probability of a crossover function is given by, $(p_2 = 1 - p_1)$. The crossover function swaps the $\alpha$ and $\beta$ spin parts of the Slater determinant. It should be noted at this point that the GACI implemented deals only with singlet states (i.e., where the number of $\alpha$ and $\beta$ electrons are identical) due to the complexity of the crossover function. This issue will be dealt with in more details in later work and generalized for all spin states. Thus, if we expand two old generation Slater determinant as,

$$|D_{old}^1\rangle = |D_{i,\alpha}\rangle|D_{j,\beta}\rangle$$

$$|D_{old}^2\rangle = |D_{k,\alpha}\rangle|D_{l,\beta}\rangle$$

where $|D_{i,\alpha}\rangle$ and $|D_{j,\beta}\rangle$ denotes the $\alpha$ and $\beta$ parts of the Slater determinant, then the new Slater determinant after the application of the crossover operator is

$$|D_{new}^1\rangle = |D_{i,\alpha}\rangle|D_{l,\beta}\rangle$$

$$|D_{new}^2\rangle = |D_{k,\alpha}\rangle|D_{j,\beta}\rangle,$$

where superscript $old$ and $new$ denotes the Slater determinant in the old and new generations respectively. Crossover, therefore, offers a method of substantial changes in the Slater determinant. In the rest of the discussion, we have used $p_1 = p_2 = 0.5$.

**Fitness function** - The proper definition of the fitness function is crucial to the efficiency of any evolutionary algorithm. In order to estimate the efficacy of different fitness functions, we have implemented and tested two different forms of the fitness function.

**Energy of Slater determinant** - Each Slater determinant created by the various operations in the propagation step has a differential occupation of orbitals. Thus,
the simplest measure of its importance in the Hilbert space is the energy of that Slater determinant. The energy dependent fitness function is defined as,

\[ f(i) = \langle D_i | \hat{H} | D_i \rangle, \] (6)

for the Slater determinant \( D_i \).

**Absolute value of CI coefficient :** In our algorithm, each propagation step expands the basis of Slater determinants and selection again brings down the total number of determinants to the required threshold population. One can diagonalize the Hamiltonian in the expanded basis \( \langle \tilde{\Psi} | \hat{H} | \tilde{\Psi} \rangle \) in the most general case, where \( S \) is the overlap between the Slater determinant basis. The eigenvector corresponding to the lowest eigenvalue in the expanded basis \( |\tilde{\Psi}\rangle \) can be written as,

\[ |\tilde{\Psi}\rangle = \sum_i c_i |D_i\rangle. \] (7)

The fitness function corresponding to each Slater determinant \( |D_i\rangle \) is defined as,

\[ f(i) = |c_i|, \] (8)

i.e. the absolute value of the CI coefficient corresponding to that Slater determinant is used as a measure of the importance or fitness of that Slater determinant.

**Selection :** The final step of an evolutionary algorithm is a selection or death step, such that based on a certain probability the fitter Slater determinant survives and therefore, the next generation or population that is created is on an average better than the previous one, in our case lower energy. There are two procedures for the final selection or death step.

In one case, we choose the \( n \) fittest Slater determinants in a non-random fashion. This is denoted as fixed selection (FS). In the other selection procedure, we use a pair-wise tournament selection based on a priori calculated fitness functions and we denote this as tournament selection (TS). The fitness functions defined above have been used as the criterion for terminating a Slater determinant. Thus, we randomly select two Slater determinants and retain the one whose fitness is higher than the other. This process is continued till the size of the population reaches the threshold.

The pilot program for GACI is written in python. The integrals and Hamiltonians for the molecular system are used from MOLPRO quantum chemistry package. The CASSCF, MP2 and FCI results for benchmark purposes are used from the MOLPRO.

The GACI algorithm is tested for 1D Hubbard problem and for molecular system, such as bond breaking problem in water molecule. Both these test cases have been routinely used to probe the efficiency of methods to treat strongly correlated systems.

**1D Hubbard model system :** The Hubbard Hamiltonian is defined as,

\[ H = -t \sum_{i,j,\sigma} (a_{i\sigma}^\dagger a_{j\sigma} + h.c.) + U \sum_j n_{j\sigma} n_{j\sigma'}, \] (9)

where \( t \) is the transfer or hopping energy between sites, and \( U \) is the on-site Coulomb interaction energy. The number operator is defined as \( n_{j\sigma} = a_{j\sigma}^\dagger a_{j\sigma} \). The convergence with GACI with different population size of Slater determinants are shown in Fig. 3 for the three system sizes that are tested (half filled). As expected, with the increase in the size of population of Slater determinants retained, the variational GACI energy approaches the FCI limit.

**Molecular Hamiltonian :** The GACI method with fixed selection (FS) and \( |c_i| \) as the fitness function is tested for water molecule along the symmetric bond stretching mode. The FCI and GACI energies in the STO-3G basis set are plotted as a function of OH bond distance and compared to MP2 and CASSCF energies (Fig. 4). It is noticed that GACI performs much better than CASSCF and MP2 with non-parallelity errors (NPE) of 3.8 mH (20 dets) and 27.1 mH (10 dets) as compared to 87.7 mH in CASSCF and 172.7 mH in MP2. In this case, we have calculated NPE as the difference between the largest error and the smallest error within the limit of bond lengths for which the calculations are performed. Since the MP2 dissociation curve turns at large bond lengths, the actual non-parallelity error of MP2 is significantly larger than what is reported here. Comparison of the wavefunctions with GACI versus FCI shows that the overlaps (\( \langle \Psi_{GACI} | \Psi_{FCI} \rangle \)) are greater than 0.9 for the range of bond lengths (shown in supplementary information).

The comparison between the two fitness functions and selection procedures, is shown in Table I. It can be seen that the absolute value of the CI coefficient is a better
FIG. 4. Water symmetric stretching. (a) Potential energy surface (PES) of water molecule along symmetric bond breaking coordinate. Comparison of GACI with CASSCF, MP2 and FCI. (b) Error in the PES with respect to FCI along the bond dissociation curve.

TABLE I. The GACI energies (in E\textsubscript{h}) with 20 determinants are shown at the equilibrium (r\textsubscript{OH} = 1.05 Å) and one stretched geometry (r\textsubscript{OH} = 2.0 Å) for the two fitness functions and two selection procedures.

| Geometry        | Equilibrium (1.05 Å) | Stretched (2.0 Å) |
|-----------------|----------------------|-------------------|
| FCI             | -75.019739           | -74.761988        |
| GACI (CI and FS)| -75.017264           | -74.758062        |
| GACI (Energy and FS) | -75.008136       | -74.757674        |
| GACI (CI and TS)| -75.013062           | -74.756904        |
| GACI (Energy and TS) | -75.009683        | -74.757453        |

Better fitness function and fixed selection method is a slightly better technique. The reason for CI coefficient being a

FIG. 5. SC and DC denote static and dynamic correlation respectively. The FCI and GACI determinants with highest CI coefficients (|c| ≥ 0.05) are denoted as FCI-SC and GACI-SC. They overlap over each other showing that GACI captures all the determinants with large coefficients. FCI-DC and GACI-DC denotes the other determinants with smaller CI coefficients (|c| < 0.05). The GACI used is with |c| as the fitness function and fixed selection criterion. (a) The histograms of numbers of determinants versus energy of determinants at the equilibrium geometry (r\textsubscript{OH} = 1.05 Å). (b) The histograms of numbers of determinants versus energy of determinants at stretched geometry (r\textsubscript{OH} = 2.0 Å). Better fitness function can be seen from Fig. 5. It shows the distribution of the determinants of different energies and we notice that while the more important Slater determinants are typically with lower energy, there are a significant number of less important Slater determinants (with lower |c|) that are also in the same energy range. Therefore, energy cannot be a good criterion for the im-
portance of a Slater determinant.

To summarize, we have developed an evolutionary algorithm based approach to sample the important part of the Hilbert space in strongly correlated systems. It is an alternative approach to MCCI, FCI-QMC and DMRG. It has similarities with these methods as well as ACI. It can be combined with renormalization group approaches to improve the subspace search in the Hilbert space. The convergence properties of GACI can be largely improved by changing the probabilities of cloning, mutation and crossover. It can also be improved by the use of other fitness functions and selection procedures. Further generation of new Slater determinants can be made in a more efficient way using heat-bath sampling techniques.

Work is in progress to rigorously test the efficiency on these different parameters and thereby improve the convergence by improving the creation of new generation in the important part of the Hilbert space and the acceptance ratio of the new generations.

Supplementary Material
See supplementary material for the most important configurations in the GACI calculations and the overlaps between the GACI and FCI wavefunctions.

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1. K. Boguslawski, P. Tecmer, G. Barcza, O. Legenza, and M. Reiher, “Orbital entanglement in bond-formation processes,” J. Chem. Theory Comput. 9, 2959–2973 (2013).

2. P. Knowles and N. Handy, “A new determinant-based full configuration interaction method,” Chem. Phys. Lett. 111, 315–321 (1984).

3. B. O. Roos, “The complete active space self-consistent-field method and its applications in electronic structure calculations,” in Adv. Chem. Phys. (2007) pp. 399–445.

4. P. A. Malmqvist, A. Rendell, and B. O. Roos, “The restricted active space self-consistent-field method, implemented with a split graph unitary group approach,” J. Phys. Chem. 94, 5477–5482 (1990).

5. S. R. White, “Density matrix formulation for quantum renormalization groups,” Phys. Rev. Lett. 69, 2863–2866 (1992).

6. G. K.-L. Chan and S. Sharma, “The density matrix renormalization group in quantum chemistry,” Ann. Rev. Phys. Chem. 62, 465–481 (2011).

7. D. Ghosh, J. Jachmann, T. Yanai, and G. K.-L. Chan, “Orbital optimization in the density matrix renormalization group, with applications to polyenes and β-carotene,” J. Chem. Phys. 128, 144117 (2008).

8. D. Zgid and M. Nooijen, “The density matrix renormalization group self-consistent field method: Orbital optimization with the density matrix renormalization group method in the active space,” J. Chem. Phys. 128, 144116 (2008).

9. G. Moritz and M. Reiher, “Decomposition of density matrix renormalization group states into a Slater determinant basis,” J. Chem. Phys. 126, 244109 (2007).

10. R. M. Noack, and S. R. White, “Measuring orbital interaction using quantum information theory,” Chem. Phys. 323, 519–531 (2006).

11. G. Moritz, B. A. Hess, and M. Reiher, “Convergence behavior of the density-matrix renormalization group algorithm for optimized orbital orderings,” J. Chem. Phys. 122, 024107 (2005).

12. H. J. Changlani, J. M. Kinder, C. J. Umrigar, and G. K.-L. Chan, “Approximating strongly correlated wave functions with correlator product states,” Phys. Rev. B 80, 245116 (2009).

13. K. H. Marti, B. Bauer, M. Reiher, M. Troyer, and F. Verstraete, “Complete-graph tensor network states: a new fermionic wave function ansatz for molecules,” New J. Phys. 12, 103008 (2010).

14. B. Weiner and J. V. Ortiz, “Effective procedure for energy optimizing antisymmetrized geminal power states,” J. Chem. Phys. 117, 5135–5154 (2002).

15. P. A. Limacher, P. W. Ayers, P. A. Johnson, S. D. Baerdemaker, D. V. Neck, and P. Bultinck, “A new mean-field method suitable for strongly correlated electrons: Computationally facile antisymmetric products of nonorthogonal geminals,” J. Chem. Theory Comput. 9, 1394–1401 (2013).

16. C. J. Umrigar, J. Toulouse, C. Filippi, S. Sorella, and R. G. Hennig, “Alleviation of the fermion-sign problem by optimization of many-body wave functions,” Phys. Rev. Lett. 98, 110201 (2007).

17. J. Toulouse and C. J. Umrigar, “Full optimization of jastrow-slater wave functions with application to the first-row atoms and homonuclear diatomic molecules,” J. Chem. Phys. 128, 174101 (2008).

18. E. Neuscamman, C. J. Umrigar, and G. K.-L. Chan, “Optimizing large parameter sets in variational quantum monte carlo,” Phys. Rev. B 85, 045103 (2012).

19. E. Neuscamman, “The jastrow antisymmetric geminal power in hilbert space: Theory, benchmarking, and application to a novel transition state,” J. Chem. Phys. 139, 194105 (2013).

20. G. H. Booth, A. J. W. Thom, and A. Alavi, “Fermion monte carlo without fixed nodes: A game of life, death, and annihilation in Slater determinant space,” J. Chemical Physics 131, 054106 (2009).

21. A. J. W. Thom, “Stochastic coupled cluster theory,” Phys. Rev. Lett. 105, 263004 (2010).

22. J. Greer, “Monte carlo configuration interaction,” Journal of Computational Physics 146, 181–202 (1998).

23. F. A. Evangelista, “Adaptive multiconfigurational wave functions,” The Journal of Chemical Physics 140, 124114 (2014).

24. J.-J. Werner, P. J. Knowles, G. Klinzis, F. R. Manby, and M. Schütz, “Molpro: a general-purpose quantum chemistry program package,” Wiley Interdisciplinary Reviews: Computational Molecular Science 2, 242–253 (2012).

25. A. A. Holmes, N. M. Tubman, and C. J. Umrigar, “Heat-bath configuration interaction: An efficient selected configuration interaction algorithm inspired by heat-bath sampling,” J. Chem. Theory Comput. 12, 3674–3680 (2016).