Towards an efficient description of strongly correlated electrons with mean-field cost

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We present an efficient approach to the electron correlation problem that is well-suited for strongly interacting many-body systems, but requires only mean-field-like computational cost. The performance of our approach is illustrated for the one-dimensional Hubbard model with periodic boundary conditions for different chain lengths, and for the non-relativistic quantum chemical Hamiltonian exploring the symmetric dissociation of the H$_{50}$ hydrogen chain.

The accurate description of the electron–electron interaction at the quantum-mechanical level is a key problem in condensed matter physics [1, 2] and quantum chemistry [3, 4]. Since most of the quantum many-body problems are extraordinarily difficult to solve exactly, different approximation schemes emerged [5–9], among which the density matrix renormalization group (DMRG) algorithm [10–12] gained a lot of popularity in both condensed matter physics [11] and quantum chemistry [13–19] over the last decade. Since the DMRG algorithm optimizes a matrix product state wavefunction, it is optimally suited for one-dimensional systems; though DMRG studies on higher-dimensional and compact systems have been reported [13, 16, 18, 20]. Yet, novel theoretical approaches are desirable that can accurately describe strong correlation effects between electrons where the dimension of the Hilbert space exceeds the present-day limit of DMRG or general tensor-network approaches [21] allowing approximately 100 sites or 60 (spatial) orbitals, respectively.

Another promising approach, suitable for larger strongly-correlated electronic systems, uses geminals (two-electron basis functions) as building blocks for the wavefunction [22–28]. One of the simplest practical geminal approaches is the antisymmetric product of 1-reference-orbital geminals (AP1roG) [29–31]. Unique among geminal methods, AP1roG can be rewritten as a fully general pair-coupled-cluster wavefunction, i.e.

$$|\Psi_{AP1roG}\rangle = \exp \left( \sum_{i=1}^{P} \sum_{a=P+1}^{K} c_{i}^{a\sigma} a_{i\sigma}^{\dagger} a_{a\sigma}^{\dagger} a_{a\sigma} a_{i\sigma} \right) |\Phi_{0}\rangle,$$

where $a_{i\sigma}$ and $a_{a\sigma}$ ($\sigma = \downarrow, \uparrow$) are the fermionic creation and annihilation operators, and $|\Phi_{0}\rangle$ is some independent-particle wave function (usually the Hartree–Fock determinant). Indices $i$ and $a$ correspond to virtual and occupied sites (orbitals) with respect to $|\Phi_{0}\rangle$. $P$ and $K$ denote the number of electron pairs ($P = N/2$ with $N$ being the total number of electrons) and orbitals, respectively, and $\{c_{i}^{a}\}$ are the geminal coefficients. This wavefunction ansatz is size-extensive and has mean-field scaling, $O(P^2(K - P)^2)$ for the projected Schrödinger equation approach [29].

To ensure size-consistency, however, it is necessary to optimize the one-electron basis functions [29], where all non-redundant orbital rotations span the occupied–occupied, occupied–virtual, and virtual–virtual blocks with respect to the reference Slater determinant $|\Phi_{0}\rangle$. We have implemented a quadratically convergent algorithm: we minimize the energy with respect to the choice of the one-particle basis functions, subject to the constraint that the projected Schrödinger equations for the geminal coefficients hold. Specifically, we use a Newton–Raphson optimizer and a diagonal approximation to the orbital Hessian to obtain the rotated set of orbital expansion coefficients. Our algorithm is analogous to the orbital-optimized coupled cluster approach [32–34]. Due to the four-index transformation of the electron repulsion integrals, the computational scaling deteriorates to $O(K^5)$. The orbital-optimized AP1roG (OO-AP1roG) approach...
was implemented in a developer version of the HORTON program package [35], and tested for (a) the half-filled one-dimensional (1-D) Hubbard Hamiltonian and (b) for the non-relativistic quantum chemical Hamiltonian.

(a) First, we consider the 1-D Hubbard model with periodic boundary conditions,

$$
\hat{H}_\text{Hub} = -t \sum_{j,\sigma} (a_{j+1,\sigma}^{\dagger} a_{j,\sigma} + a_{j,\sigma}^{\dagger} a_{j+1,\sigma}) + U \sum_j n_{j\uparrow} n_{j\downarrow},
$$

where the first term represents nearest-neighbor hopping and the second term is the repulsive on-site interaction. The operators $a_{j,\sigma}^{\dagger}$ and $a_{j,\sigma}$ are again the fermionic creation and annihilation operators on a lattice with sites $j = 1,...,N_{\text{sites}}$, and $n_{j\sigma} = a_{j,\sigma}^{\dagger} a_{j,\sigma}$ is the local number operator.

We start our discussion by analyzing the half-filled 1-D Hubbard model. Figure 1 shows the differences in total energies obtained for OO-AP1roG with respect to reference data obtained from the solution of the Lieb-Wu equations [36] ($N_{\text{sites}} = 6, 10, 14, 50, 122$). OO-AP1roG can reproduce the exact total energies in the limit of zero and infinite (repulsive) on-site interaction. The largest deviations from the exact solution (up to 0.08$t$ per site) are found for the intermediate region of the on-site interaction, that is, for $2t < U < 50t$. Figure 2 shows the percentage of the correlation energy captured by OO-AP1roG in the half-filled 1-D Hubbard model with $N_{\text{sites}} = 6, 10, 14, 50, 122$ captured by OO-AP1roG. The exact values for small $U$ ($U < 0.001t$) for $N_{\text{sites}} = 50, 122$ could not be converged.

(b) The non-relativistic quantum chemical Hamiltonian for different strengths of the repulsive on-site interaction in the half-filled 1-D Hubbard model with $N_{\text{sites}} = 6, 10, 14, 50, 122$ is visualized in Figure 3 for four different on-site repulsive interaction strengths. For small values of $U$, the geminal coefficient matrix correctly approaches the zero matrix indicating that a single Slater determinant is sufficient to describe the quantum state exactly. For increasing $U$, the geminal coefficient matrix becomes diagonal and approaches perfect pairing (seniority-zero) wavefunction [37, 38],

$$
\prod_{i=1,3,...} \langle (a_{i,\uparrow}^{\dagger} + a_{i+1,\uparrow}^{\dagger})(a_{i,\downarrow}^{\dagger} + a_{i+1,\downarrow}^{\dagger}) - (a_{i,\uparrow}^{\dagger} - a_{i+1,\uparrow}^{\dagger})(a_{i,\downarrow}^{\dagger} - a_{i+1,\downarrow}^{\dagger})\rangle |0\rangle
$$

Table 1 lists the ground-state ($E$) and correlation ($\kappa$) energies of half-filled 1-D lattices of different lengths obtained from OO-AP1roG. For each chain length, three different values of $U$, $U = 2t, 4t$ and $8t$, representing weak, intermediate and strong electron-electron interaction, respectively, have been chosen and compared with the corresponding exact solutions [39, 40]. OO-AP1roG can recover about 71% of the correlation energy in the weak interaction regime, about 80% for intermediate interaction strengths, and approximately 93% in the case of strong on-site interaction for all chain lengths studied, but has mean-field-like scaling. We should emphasize that the amount of correlation energy captured by OO-AP1roG does not depend on the chain length (cf. Figures 1 and 2), which underlines the size-consistency of the approach.

The geminal coefficient matrix $\{c_i^\alpha\}$ for $N_{\text{sites}} = 14$ is visualized in Figure 3 for four different on-site repulsive interaction strengths. For small values of $U$, the geminal coefficient matrix is sparse and thus far from perfect pairing, which is represented by a diagonal geminal coefficient matrix. In the limit $U \to 0$, the geminal coefficient matrix correctly approaches the zero matrix indicating that a single Slater determinant is sufficient to describe the quantum state exactly. For increasing $U$, the geminal coefficient matrix becomes diagonal-dominant and adopts a diagonal structure in the limit of $U \to \infty$. Thus, in the limit of infinite (repulsive) interaction, OO-AP1roG optimizes a perfect-pairing (seniority-zero) wavefunction [37, 38].
TABLE I. Ground-state (E) and correlation (κ) energies of half-filled 1-D lattices with \( N_{\text{sites}} = 30, 50 \) and 122 in units of \( t \). Comparison of the OO-AP1roG approach with exact values.

| \( N_{\text{sites}} \) | \( U \) | \( U = 2t \) | \( U = 4t \) | \( U = 8t \) | \( U = 2t \) | \( U = 4t \) | \( U = 8t \) | Exact | Exact |
|---|---|---|---|---|---|---|---|---|---|
| 30 | \( U \) | \( -23.2671 \) | \( -24.7614 \) | \( -1.4943 \) | \( 70.6 \) | \( -25.3835 \) | \( -2.1164 \) | |
| 30 | \( 8t \) | \( 21.7329 \) | \( -7.7639 \) | \( -29.4968 \) | \( 93.4 \) | \( -9.8387 \) | \( -31.5716 \) | |
| 50 | \( U \) | \( -38.7039 \) | \( -41.2481 \) | \( -2.5442 \) | \( 71.9 \) | \( -42.2443 \) | \( -3.5404 \) | |
| 50 | \( 4t \) | \( -13.7039 \) | \( -25.2718 \) | \( -11.5679 \) | \( 77.1 \) | \( -28.6993 \) | \( -14.9554 \) | |
| 50 | \( 8t \) | \( 36.2961 \) | \( -12.8277 \) | \( -49.1238 \) | \( 93.2 \) | \( -16.3842 \) | \( -52.6803 \) | |
| 122 | \( U \) | \( -94.3524 \) | \( -100.5018 \) | \( -6.1494 \) | \( 70.9 \) | \( -103.9221 \) | \( -6.6687 \) | |
| 122 | \( 4t \) | \( -33.3524 \) | \( -62.9752 \) | \( -29.6228 \) | \( 80.8 \) | \( -70.0003 \) | \( -36.6479 \) | |
| 122 | \( 8t \) | \( 88.6476 \) | \( -31.0294 \) | \( -119.6770 \) | \( 93.1 \) | \( -39.9619 \) | \( -128.6095 \) | |

FIG. 3. Evolution of the geminal matrix coefficients \( \{c^a_\sigma\} \) for different strengths of the repulsive on-site interaction in the half-filled 1-D Hubbard model with \( N_{\text{sites}} = 14 \).

The Hamiltonian in its second quantized form reads

\[
\hat{H} = \sum_{pq,\sigma} \hbar q p a^\dagger_{pq} a_{pq} + \frac{1}{2} \sum_{pqrs,\sigma\tau} \langle pq|rs\rangle a^\dagger_{pq} a_{qr} a_{sr} a_{r\tau} + H_{\text{nuc}},
\]

(4)

where the first term comprises the kinetic energy and nuclear–electron attraction, the second term is the electron-electron interaction, and the third term represents the nuclear–nuclear repulsion energy, respectively. In Eq. (4), indices \( p, q, r \) and \( s \) run over all one-particle basis functions, while \( \sigma \) and \( \tau \) denote the electron spin (\( \{\uparrow, \downarrow\} \)). The Hamiltonian as defined in Eq. (4) was used for the study of the symmetric stretching of the \( \text{H}_5 \) hydrogen chain, which is a commonly-used molecular model for strongly-correlated systems and which remains a challenging problem for conventional quantum-chemistry methods [41–44].

In Figure 4 the performance of AP1roG and OO-AP1roG is compared to restricted Hartree–Fock (RHF), second-order Möller-Plesset (MP2) perturbation theory, coupled cluster theory with singles, doubles and perturbative triples (CCSD(T)), and density functional theory using the PBE [46] exchange–correlation functional. As reference, the DMRG potential energy curve determined in Ref. [41] was used, which can be considered as the exact-diagonalization limit. None of the standard quantum chemical methods, like MP2, CCSD(T) or DFT using the PBE exchange–correlation functional, yield qualitatively correct energy curves for the symmetric stretching of the \( \text{H}_5 \) chain. In particular, the potential energy depth determined from DFT and MP2 is too deep, while CCSD(T) does not converge for interatomic distances larger than 2.0 Å. Note that the lack of size-consistency in AP1roG is cured by orbital optimization in the OO-AP1roG approach. The latter yields a potential energy curve that is closest to the DMRG reference data along the whole dissociation pathway and leads to a proper dissociation limit of \( \text{H}_5 \).

Wavefunctions constructed as antisymmetric products of nonorthogonal geminals, like the AP1roG wavefunction scrutinized here, provide an alternative approach to electronic structure, with mean-field scaling. Because
it uses electron pairs as a building block. AP1roG is a suitable way to describe strong correlations dominated by electron pairing. However, in order to ensure size-consistency, the single-particle (orbital) basis used to construct the electron pairs must be optimized. Our results show that orbital-optimized AP1roG is a robust and exactly-solvable models with Peter Limacher and Paul Johnson.

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