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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 and quantum chemistry. 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 [13–20] 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 [14, 17, 19, 21]. 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 [22] 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 [23–30]. One of the simplest practical geminal approaches is the antisymmetric product of 1-reference-orbital geminals (AP1roG) [31–33]. Unique among geminal methods, AP1roG can be rewritten as a fully general pair-coupled-cluster doubles wavefunc-

tion [34], i.e.

$$|\Psi_{\text{AP1roG}}\rangle = \exp\left(\sum_{i=1}^P \sum_{a=P+1}^K c_i^a a_{a\uparrow}^\dagger a_{a\downarrow}^\dagger a_{i\downarrow} a_{i\uparrow}\right) |\Phi_0\rangle, \quad (1)$$

where $a_{p\sigma}^\dagger$ and $a_{p\sigma}$ ($\sigma = \downarrow, \uparrow$) are the fermionic creation and annihilation operators, and $|\Phi_0\rangle$ is some independent-particle wavefunction (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, $\mathcal{O}(P^2(K - P)^2)$ for the projected Schrödinger equation approach [31].

To ensure size-consistency, however, it is necessary to optimize the one-electron basis functions [31], 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 of the orbital Hessian to obtain the rotated set of orbital expansion coefficients. Our algorithm is analogous to the orbital-optimized coupled cluster approach [35–37]. Due to the four-index transformation of the electron repulsion integrals, the computational scaling deteriorates to $\mathcal{O}(K^5)$. The orbital-optimized AP1roG (OO-AP1roG) approach was implemented in a developer version of the

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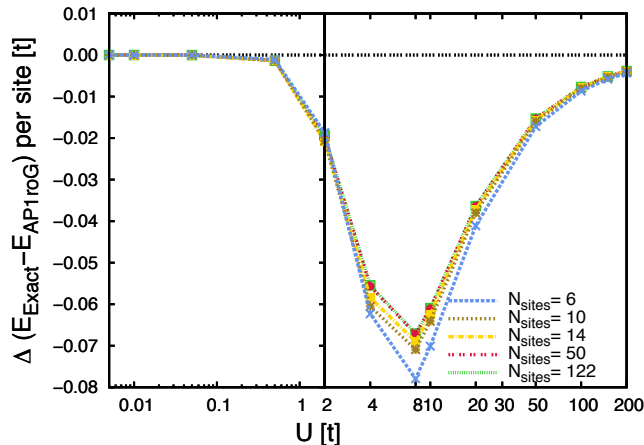


FIG. 1. Deviation of the OO-AP1roG total energies from exact values (blue dashed line) for different strengths of the repulsive on-site interaction for the 1-D Hubbard model (with periodic boundary conditions) for $N_{\text{sites}} = 6, 10, 14, 50, 122$. The exact values for small U ($U < 0.001t$) for $N_{\text{sites}} = 50, 122$ could not be converged.

HORTON program package [38].

(a) The half-filled one-dimensional Hubbard Hamiltonian. First, we consider the 1-D Hubbard model Hamiltonian with periodic boundary conditions,

$$\hat{H}_{\text{Hub}} = -t \sum_{j,\sigma} \left(a_{(j+1)\sigma}^\dagger a_{j\sigma} + a_{j\sigma}^\dagger a_{(j+1)\sigma} \right) + U \sum_j n_{j\uparrow} n_{j\downarrow}, \quad (2)$$

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 $j = 1, \dots, N_{\text{sites}}$, and $n_{j\sigma} = a_{j\sigma}^\dagger a_{j\sigma}$ is the local number operator.

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 [39] ($N_{\text{sites}} = 6, 10, 14, 50, 122$). 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 $0.075t$ 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 calculated as $\% \kappa = \frac{E^{\text{OO-AP1roG}} - E^{\text{HF}}}{E^{\text{exact}} - E^{\text{HF}}} \cdot 100$. In the limit of zero and infinite U , the OO-AP1roG model becomes exact; for $U = 0$ the wavefunction can be exactly described by a single Slater determinant and thus the correlation energy approaches zero, while for $U \rightarrow \infty$, the quantum state can be represented by the perfect pairing wavefunction. For growing (repulsive) U , the percentage of the correlation energy covered by OO-AP1roG increases gradually.

For small values of U , the geminal coefficient matrix $\{c_i^a\}$ is sparse and thus far from perfect pairing, which is represented by a diagonal geminal coefficient matrix

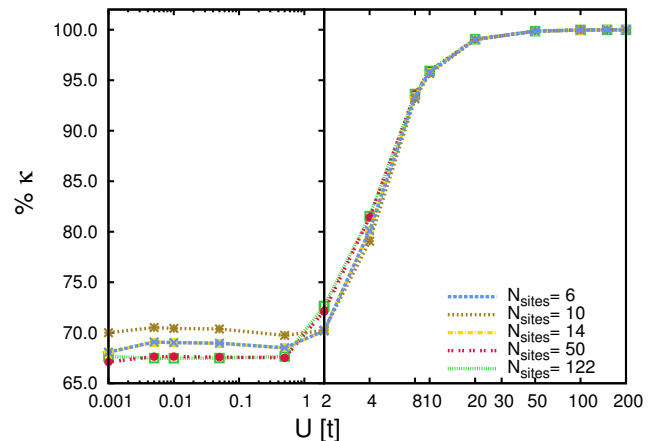


FIG. 2. Percentage of the correlation energy $\% \kappa$ for different strengths of the repulsive on-site interaction in the half-filled 1-D Hubbard model (with periodic boundary conditions) for $N_{\text{sites}} = 6, 10, 14, 50, 122$ captured by OO-AP1roG. The exact values for small U ($U < 0.001t$) for $N_{\text{sites}} = 50, 122$ could not be converged.

(see Figure I in the Supplementary Information). In the limit $U \rightarrow 0$, 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 , $\{c_i^a\}$ becomes diagonal-dominant and adopts a diagonal structure in the limit of $U \rightarrow \infty$. Thus, in the limit of infinite (repulsive) interaction, OO-AP1roG optimizes a perfect-pairing (seniority-zero) wavefunction [40, 41],

$$\prod_{i=1,3,\dots} [(a_{i,\uparrow}^\dagger + a_{i+1,\uparrow}^\dagger)(a_{i,\downarrow}^\dagger + a_{i+1,\downarrow}^\dagger) - (a_{i,\uparrow}^\dagger - a_{i+1,\uparrow}^\dagger)(a_{i,\downarrow}^\dagger - a_{i+1,\downarrow}^\dagger)] |0\rangle \quad (3)$$

To conclude, OO-AP1roG has mean-field-like scaling, but 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 (a numerical comparison is presented in Table I of the Supplementary Information).

Figure 3 shows the single-orbital entropy for different lengths of the 1-D lattice as a function of the repulsive on-site interaction U . The single-orbital entropy is the analogue of the one-site entropy, but determined in the natural orbital basis: it is calculated as the von Neumann entropy from a single-orbital density matrix (a many-particle reduced density matrix of one orbital). It measures the entanglement of one orbital with the remaining $(N_{\text{sites}} - 1)$ ones [18]. In particular, since the optimized orbitals are localized on two neighboring sites, the von Neumann entropy describes the correlation of a pair of sites and the other part of the system. In the following, we will refer to the single-orbital entropy as the pair entanglement E_p in accordance with the local entanglement determined for the on-site basis [44].

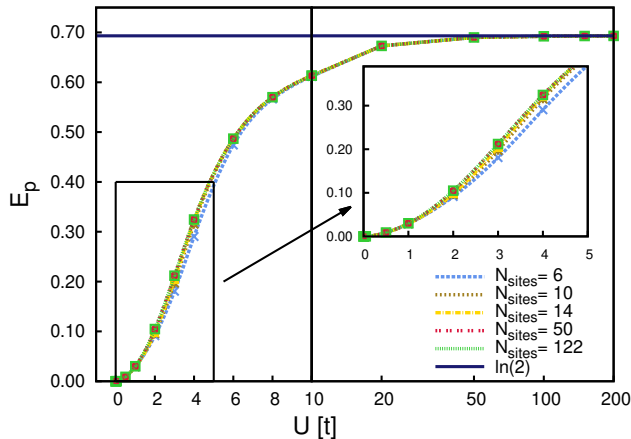


FIG. 3. Pair entanglement E_p (single-orbital entropy) for different strengths of the repulsive on-site interaction in the half-filled 1-D Hubbard model (with periodic boundary conditions) for $N_{\text{sites}} = 6, 10, 14, 50, 122$ calculated by OO-AP1roG.

The pair entanglement takes its minimum value at $U = 0t$ where the wavefunction can be exactly represented by a single Slater determinant. It is easy to verify that all orbital pairs are uncorrelated in a one-determinant wavefunction and thus $E_p = 0$. For increasing on-site interaction, the pair entanglement smoothly accumulates (see Figure 3) and reaches its maximum value of $\ln 2$ in the large U limit (for $U \rightarrow \infty$, the single-orbital density matrix has the diagonal elements $\{0, 0, 0.5, 0.5\}$). Note that OO-AP1roG yields similar pair entanglement profiles for all chain lengths studied and correctly reproduces the small and large U limits.

(b) Symmetric dissociation of the H_{50} molecule.

The non-relativistic quantum chemical Hamiltonian in its second quantized form reads

$$\hat{H} = \sum_{pq,\sigma} h_{pq} a_{p\sigma}^\dagger a_{q\sigma} + \frac{1}{2} \sum_{pqrs,\sigma\tau} \langle pq|rs \rangle a_{p\sigma}^\dagger a_{q\tau}^\dagger a_{s\tau} a_{r\sigma} + H_{\text{nuc}}, \quad (4)$$

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 σ and τ denote the electron spin ($\{\uparrow, \downarrow\}$). The Hamiltonian as defined in Eq. (4) was used for the study of the symmetric stretching of the H_{50} hydrogen chain, which is a commonly-used molecular model for strongly-correlated systems and which remains a challenging problem for conventional quantum-chemistry methods [45–48].

In Figure 4, the performance of AP1roG and OO-AP1roG is compared to restricted Hartree-Fock (RHF), second-order Møller-Plesset (MP2) perturbation theory, coupled cluster theory with singles, doubles and perturbative triples (CCSD(T)), and density functional theory using the PBE [50] exchange-correlation functional. As

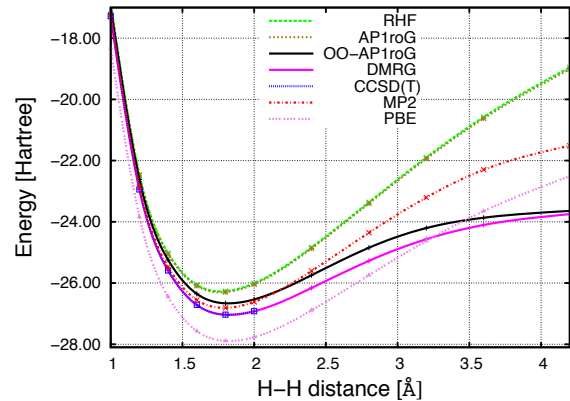


FIG. 4. Symmetric dissociation of H_{50} chain using the STO-6G basis set [49] obtained from different methods. The DMRG reference data are taken from Ref. 45.

TABLE I. Spectroscopic constants: equilibrium bond distance (R_e), potential energy depth (D_e) and harmonic vibrational frequency (ω_e) for the ground state of H_{50} (STO-6G). Differences with respect to the DMRG reference data are listed in parenthesis.

Method	R_e [Å]	D_e [eV]	ω_e [cm^{-1}]
RHF	0.940 (−0.030)	199.0 (+109.3)	25089 (+2268)
AP1roG	0.941 (−0.029)	198.2 (+108.5)	23013 (+2252)
MP2	0.955 (−0.015)	144.1 (+54.4)	24568 (+1747)
PBE	0.971 (+0.001)	146.6 (+56.9)	23662 (+841)
OO-AP1roG	0.966 (−0.004)	82.2 (−7.5)	23013 (+192)
DMRG [45]	0.970	89.7	22821

reference, the DMRG potential energy curve determined in Ref. 45 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 H_{50} 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 H_{50} . Moreover, the OO-AP1roG method gives spectroscopic constants (presented in Table I) that are in excellent agreement with DMRG reference data, outperforming standard quantum-chemistry approaches.

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 method all the way from the weakly-correlated to the strongly-correlated limit, in both molecules and periodic systems.

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