

Analysis of two-orbital correlations in wave functions restricted to electron-pair states

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Wave functions constructed from electron-pair states can accurately model strong electron correlation effects and are promising approaches especially for larger many-body systems. In this article, we analyze the nature and the type of electron correlation effects that can be captured by wave functions restricted to electron-pair states. We focus on the pair-coupled-cluster doubles (pCCD) ansatz also called the antisymmetric product of the 1-reference orbital geminal (AP1roG) method, combined with an orbital optimization protocol presented in Boguslawski *et al.* [Phys. Rev. B **89**, 201106(R) (2014)], whose performance is assessed against electronic structures obtained from density-matrix renormalization-group reference data. Our numerical analysis covers model systems for strong correlation: the one-dimensional Hubbard model with a periodic boundary condition as well as metallic and molecular hydrogen rings. Specifically, the accuracy of pCCD/AP1roG is benchmarked using the single-orbital entropy, the orbital-pair mutual information, as well as the eigenvalue spectrum of the one-orbital and two-orbital reduced density matrices. Our study indicates that contributions from singly occupied states become important in the strong correlation regime which highlights the limitations of the pCCD/AP1roG method. Furthermore, we examine the effect of orbital rotations within the pCCD/AP1roG model on correlations between orbital pairs.

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I. INTRODUCTION

The many-electron problem remains one of the main challenges of quantum physics and quantum chemistry. It originates from the fact that electrons do not move independently but in a correlated fashion. A quantum description of these effects requires solving the many-body Schrödinger equation for which exact solutions are known only for some model systems [1–3]. In practice, we have to rely on approximate methods [4]. However, many approximate numerical algorithms scale exponentially with system size if the quantum system contains strongly correlated electrons. The most promising numerical approaches to treat strongly correlated fermions are the density-matrix renormalization-group (DMRG) algorithm [5–15] and the quantum Monte Carlo method [16–18].

Another approach to accurately model strongly correlated electronic systems uses geminals (two-electron basis functions) as building blocks for the electronic wave function [19–26]. In contrast to geminal-based methods, conventional approaches, such as DMRG, exploit one-electron functions (orbitals) to model many-body quantum systems. In its second-quantized form, a geminal wave function can be written as

$$|\text{geminal}\rangle = \psi_1^\dagger \psi_2^\dagger \cdots \psi_{N/2}^\dagger |0\rangle, \quad (1)$$

with N being the number of electrons, $|0\rangle$ denoting the vacuum state with respect to the creation of the geminals, and ψ_i^\dagger is a correlated two-electron function (a geminal). If we restrict geminals to be singlet functions, a pair creation in its natural

form, then reads

$$\psi_i^\dagger = \sum_{p=1}^{M_i} c_p^i a_{p\uparrow}^\dagger a_{p\downarrow}^\dagger, \quad (2)$$

where M_i is the number of one-particle functions (the natural orbitals) used to create geminal i , c_p^i is a geminal matrix coefficient for subspace M_i and $a_{p\uparrow}^\dagger$ and $a_{p\downarrow}^\dagger$ are the standard electron creation operators for up- and down-spin electrons (\uparrow, \downarrow). The structure of the geminal coefficient matrix $\{c_p^i\}$ depends on the geminal wave-function ansatz used. Thus, restricting $\{c_p^i\}$, we can derive different flavors for geminal-model wave functions [27]. The most popular approaches are based on the antisymmetric product of strongly orthogonal geminals [19,28–33], the antisymmetrized geminal power [20,34–36] (which is a special case of projected Hartree-Fock-Bogoliubov [37]), the antisymmetric product of interacting geminals [21,25,38–42], or the antisymmetric product of 1-reference-orbital geminals (AP1roG) [27,43]. Specifically, the AP1roG model allows us to approximate the doubly occupied configuration interaction (DOCI) [44] wave function but requires only mean-field computational cost in contrast to the factorial scaling of traditional DOCI implementations. For AP1roG, the sum of Eq. (3) is restricted to run over one occupied orbital i of some reference determinant and all unoccupied orbitals a ,

$$\psi_i^\dagger = a_{i\uparrow}^\dagger a_{i\downarrow}^\dagger + \sum_{a=P+1}^K c_a^i a_{a\uparrow}^\dagger a_{a\downarrow}^\dagger, \quad (3)$$

where P is the number of electron pairs ($P = N/2$ with N being the total number of electrons) and K is the total number of basis functions.

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This ansatz for ψ_i^\dagger allows us to rewrite the AP1roG wave function as a pair-coupled-cluster doubles (pCCD) wave function [45,46], i.e.,

$$|\text{AP1roG}\rangle = \exp\left(\sum_{i=1}^P \sum_{a=P+1}^K c_i^a a_{a\uparrow}^\dagger a_{a\downarrow}^\dagger a_{i\downarrow} a_{i\uparrow}\right) |\Phi_0\rangle, \quad (4)$$

where $|\Phi_0\rangle$ is some reference determinant. Indices i and a correspond to occupied and virtual sites (orbitals) with respect to $|\Phi_0\rangle$ and P and K again denote the number of electron pairs and orbitals, respectively. The geminal coefficients $\{c_i^a\}$ thus correspond to the (pair-) coupled-cluster amplitudes. Extensions to the original pCCD ansatz where the cluster operator is still restricted to electron-pair excitations have been proposed as well (see for instance the pair-extended CCD approach [47]). The AP1roG/pCCD wave-function ansatz is, by construction, size extensive and has mean-field scaling if the geminal coefficients are optimized using the projected Schrödinger equation approach. Note that $|\Phi_0\rangle$ is optimized as well and hence differs from the Hartree-Fock determinant. In the following, we will use the acronym AP1roG instead of pCCD.

Recent studies demonstrate that AP1roG can reliably model strongly correlated systems [48–53], even heavy-element-containing molecules with multiple degenerate single-particle states [52]. However, most of the analysis presented so far was based on energetic arguments or one-body correlation functions, such as occupation numbers. In this paper, we will present an in-depth analysis of orbital-pair correlations captured by the AP1roG model for one-dimensional (1D) systems where quantum fluctuations have a more pronounced role. Specifically, we will use concepts of quantum information theory to assess orbital entanglement and orbital-pair correlations [13,54–60], which are particularly instructive to dissect electron correlation effects [55,57], elucidate chemical reactions [52,58,61–65], detect changes in the electronic wave function [66–68], and define active orbital spaces [59,69–71].

The entanglement entropy of orbital i , also called single-orbital entropy, can be calculated from the eigenvalues of the one-orbital reduced density-matrix (RDM) $\omega_{\alpha;i}$ [72],

$$s_i = -\sum_{\alpha=1}^4 \omega_{\alpha;i} \ln \omega_{\alpha;i}. \quad (5)$$

The single-orbital entropy is thus the von Neumann entropy of the reduced density matrix of the orbital of interest whose elements can be calculated from the one- and two-particle reduced density matrices [59] γ_q^p and Γ_{rs}^{pq} where for a given wave function $|\Psi\rangle$,

$$\gamma_q^p = \frac{\langle \Psi | a_p^\dagger a_q | \Psi \rangle}{\langle \Psi | \Psi \rangle}, \quad (6)$$

and

$$\Gamma_{rs}^{pq} = \frac{\langle \Psi | a_p^\dagger a_q^\dagger a_s a_r | \Psi \rangle}{\langle \Psi | \Psi \rangle}, \quad (7)$$

or from generalized correlation functions [56,58]. The one-orbital reduced density-matrix ρ_i is spanned by the basis states of the one-orbital Fock space and is thus a 4×4 matrix.

Similarly, the entanglement of two orbitals is quantified by the two-orbital entropy $s_{i,j}$,

$$s_{i,j} = -\sum_{\alpha=1}^{16} \omega_{\alpha;i,j} \ln \omega_{\alpha;i,j}, \quad (8)$$

where $\omega_{\alpha;i,j}$ are the eigenvalues of the two-orbital reduced density-matrix $\rho_{i,j}$, which is defined in terms of basis states of a two-orbital Fock space (16 possible states in the case of spatial orbitals [73]). In contrast to ρ_i , the matrix elements of $\rho_{i,j}$ can be written in terms of the elements of the one-, two-, three-, and four-particle reduced density-matrices γ_q^p , Γ_{rs}^{pq} , Γ_{stu}^{pqr} , and Γ_{tuvw}^{pqrs} , with

$$\Gamma_{stu}^{pqr} = \frac{\langle \Psi | a_p^\dagger a_q^\dagger a_r^\dagger a_u a_t a_s | \Psi \rangle}{\langle \Psi | \Psi \rangle}, \quad (9)$$

and

$$\Gamma_{tuvw}^{pqrs} = \frac{\langle \Psi | a_p^\dagger a_q^\dagger a_s^\dagger a_w a_v a_u a_t | \Psi \rangle}{\langle \Psi | \Psi \rangle}. \quad (10)$$

Given s_i and $s_{i,j}$, we can quantify the correlations between two orbitals i and j by the orbital-pair mutual information [54,72,73],

$$I_{i|j} = s_i + s_j - s_{i,j}, \quad (11)$$

which includes correlations of both classical and quantum origins. The mutual information measures pairwise correlations. In this paper, we will employ the orbital-pair mutual information as a correlation index to quantify orbital-pair correlations embedded in wave functions constructed from electron-pair states.

This paper is organized as follows. In Sec. II, we briefly summarize how the one- and two-orbital reduced density matrices can be calculated for seniority-zero wave functions, that is, wave functions restricted to electron-pair states. Numerical examples are presented in Sec. III for the one-dimensional Hubbard model with periodic boundary conditions and in Sec. IV for hydrogen rings. Finally, we conclude in Sec. V.

II. CORRELATION FUNCTIONS FOR SENIORITY-ZERO WAVE FUNCTIONS

If the electronic wave function is a CI expansion with pair-excited Slater determinants only, that is, a seniority-zero wave function, then ρ_i and $\rho_{i,j}$ have a particular simple form [59]. Restricting the wave-function expansion to either doubly occupied or unoccupied orbitals, ρ_i reduces to a 2×2 matrix, whereas $\rho_{i,j}$ becomes a 4×4 matrix. Furthermore, for seniority-zero wave functions, we can use the relations $\gamma_{\bar{p}}^p = \gamma_{\bar{p}}^{\bar{p}} = \Gamma_{\bar{p}\bar{p}}^{p\bar{p}}$ and $\Gamma_{\bar{p}\bar{q}}^{p\bar{q}} = {}^4\Gamma_{\bar{p}\bar{p}\bar{q}\bar{q}}^{p\bar{p}q\bar{q}}$ [44] (\bar{p} is equivalent to p_\downarrow) so that only the one- and two-particle reduced density matrices are required to determine ρ_i and $\rho_{i,j}$. Specifically, we have [59]

$$\rho_i = \begin{pmatrix} 1 - \gamma_i^i & 0 \\ 0 & \gamma_i^i \end{pmatrix} \quad (12)$$

for the seniority-zero one-orbital RDM expressed in the basis $\{-, \uparrow\}$, and

$$\rho_{j,i} = \begin{pmatrix} 1 - \gamma_i^i - \gamma_j^j + \Gamma_{ji}^{ji} & 0 & 0 & 0 \\ 0 & \gamma_i^i - \Gamma_{ji}^{ji} & \Gamma_{ji}^{ji} & 0 \\ 0 & \Gamma_{ji}^{ji} & \gamma_j^j - \Gamma_{ji}^{ji} & 0 \\ 0 & 0 & 0 & \Gamma_{ji}^{ji} \end{pmatrix} \quad (13)$$

for the seniority-zero two-orbital RDM expressed in the basis $\{-, -, \uparrow, \uparrow\}$. We should note that, for a seniority-zero wave function, the maximum value of s_i is $\ln(2)$.

For AP1roG, the response one- and two-particle RDMs are used to construct ρ_i and $\rho_{i,j}$ and are defined as

$$\gamma_q^p = \langle \Phi_0 | (1 + \Lambda) e^{-\hat{T}_p} \{a_p^\dagger a_q\} e^{\hat{T}_p} | \Phi_0 \rangle, \quad (14)$$

and

$$\Gamma_{rs}^{pq} = \langle \Phi_0 | (1 + \Lambda) e^{-\hat{T}_p} \{a_p^\dagger a_q^\dagger a_s a_r\} e^{\hat{T}_p} | \Phi_0 \rangle, \quad (15)$$

where $\Lambda = \sum_{ia} \lambda_a^i a_i^\dagger a_{\bar{a}} a_a$ is a deexcitation operator and \hat{T}_p is restricted to pair excitations only [cf. Eq. (4)]. Explicit formulas for γ_q^p and Γ_{rs}^{pq} can be found in Refs. [74,75]. Furthermore, due to the special structure of the wave function, the only nonzero elements are γ_p^p , Γ_{pq}^{pq} , and Γ_{pp}^{qq} . We should note that the response density matrices are not Hermitian and, in general, we have $\Gamma_{pp}^{qq} \neq \Gamma_{qq}^{pp}$. The deviation from Hermiticity of the response density matrices is an artifact of the truncation of the full cluster operator and disappears if the full cluster operator is taken in the coupled-cluster ansatz. As the AP1roG method uses, however, a truncated cluster operator, we cannot exclude nonsymmetric two-particle response density matrices. Furthermore, if the response density matrices are not symmetric and are thus not N representable, the resulting eigenvalues of $\rho_{p,q}$ might result in negative values for the orbital-pair p,q . In this paper, however, we have not observed any problems with N representability of the response density matrices if the orbital basis is optimized within the AP1roG method. Only minor N -representability issues have been observed when using canonical Hartree-Fock orbitals in the strong correlation regime with negative eigenvalues on the order of 10^{-3} or much smaller (see also Supplemental Material [76]). Since negative eigenvalues are unphysical, we have discarded them when calculating the correlation functions.

III. THE HALF-FILLED ONE-DIMENSIONAL HUBBARD HAMILTONIAN

First, we consider the 1D Hubbard model Hamiltonian with periodic boundary conditions,

$$\begin{aligned} \hat{H}_{\text{Hub}} = & -t \sum_{\substack{j \\ \sigma \in \{\uparrow, \downarrow\}}} (a_{j\sigma}^\dagger a_{(j+1)\sigma} + a_{(j+1)\sigma}^\dagger a_{j\sigma}) \\ & + U \sum_j n_{j\uparrow} n_{j\downarrow}, \end{aligned} \quad (16)$$

where the first term describes nearest-neighbor hopping, whereas the second term represents the repulsive on-site interaction for $U > 0$. $n_{j\sigma} = a_{j\sigma}^\dagger a_{j\sigma}$ is the local number operator. It is well known that the one-dimensional half-filled Hubbard model for $U = 0t$ is gapless where all four local basis states $(|-\rangle|+\rangle, |\uparrow\rangle, |\downarrow\rangle, |\uparrow\downarrow\rangle)$ have equal weights $\frac{1}{4}$ and hence the site entropy $s_i = \ln(4)$. For $U > 0t$, the charge gap opens, and the weights of the unoccupied and doubly filled basis states decrease. In the large $U/t \rightarrow \infty$ limit, only the $|\uparrow\rangle$ and $|\downarrow\rangle$ states have weights of 0.5 with $s_i = \ln(2)$ as the model becomes equivalent to the spin-1/2 Heisenberg model, and the ground state is an antiferromagnetic state. Therefore, a wave function restricted to electron-pair states $(|-\rangle$ and $|\uparrow\downarrow\rangle)$ cannot properly describe the correlations in both the large U/t limit and, to a smaller extent, for small U/t using the local on-site basis. To properly model such wave functions, we have to change the basis, which allows us to describe correlations of the one-dimensional half-filled Hubbard model with only unoccupied and doubly filled basis states. Such a basis can be obtained self-consistently within the AP1roG method as, for instance, described in Refs. [43,46,49,51]. Note that correlation and entanglement measures are basis dependent and thus the one-site (orbital) and two-orbital correlations within the optimized AP1roG basis will differ from those in the local on-site basis. In order to assess the accuracy of AP1roG in describing orbital-pair correlations of the one-dimensional half-filled Hubbard model, we will perform DMRG calculations using the optimized AP1roG basis. As an example, we will only investigate the one-dimensional Hubbard model with 14 sites. The electronic energies obtained by DMRG and AP1roG as well as additional numerical examples using 30 sites are summarized in the Supplemental Material [76].

The Hubbard model in the AP1roG basis

Figure 1 shows the orbital-pair mutual information and the single-orbital entropy obtained from DMRG (left panel) and AP1roG (right panel), respectively, for different strengths of U for the optimized AP1roG basis. For all investigated values of U , AP1roG can reproduce the most important orbital correlations (cf. the black/blue lines in Fig. 1). Weaker orbital correlations ($I_{i|j} \leq 10^{-2}$) are, however, underestimated for small U/t if the wave functions are restricted to the seniority-zero sector. For increasing repulsive on-site interactions $U \geq 4t$, AP1roG gradually overestimates orbital-pair correlations compared to the DMRG reference distribution (cf. increasing number of red/blue lines). The observed overcorrelation of AP1roG for increasing U/t is also visible in the decaying values of $I_{i|j}$ shown in Fig. 2(a). Specifically, for large U/t , AP1roG features a prolonged plateau of orbital-pair correlations, in contrast to the multiple characteristic steps in $I_{i|j}$ obtained by DMRG. Thus, restricting the wave function to the seniority-zero sector results in an overestimation of the medium-sized and weak orbital-pair correlations.

To elucidate the origins of these discrepancies, we will analyze the eigenvalues and eigenvectors of the one- and two-orbital reduced density matrices ρ_i and $\rho_{i,j}$, respectively,

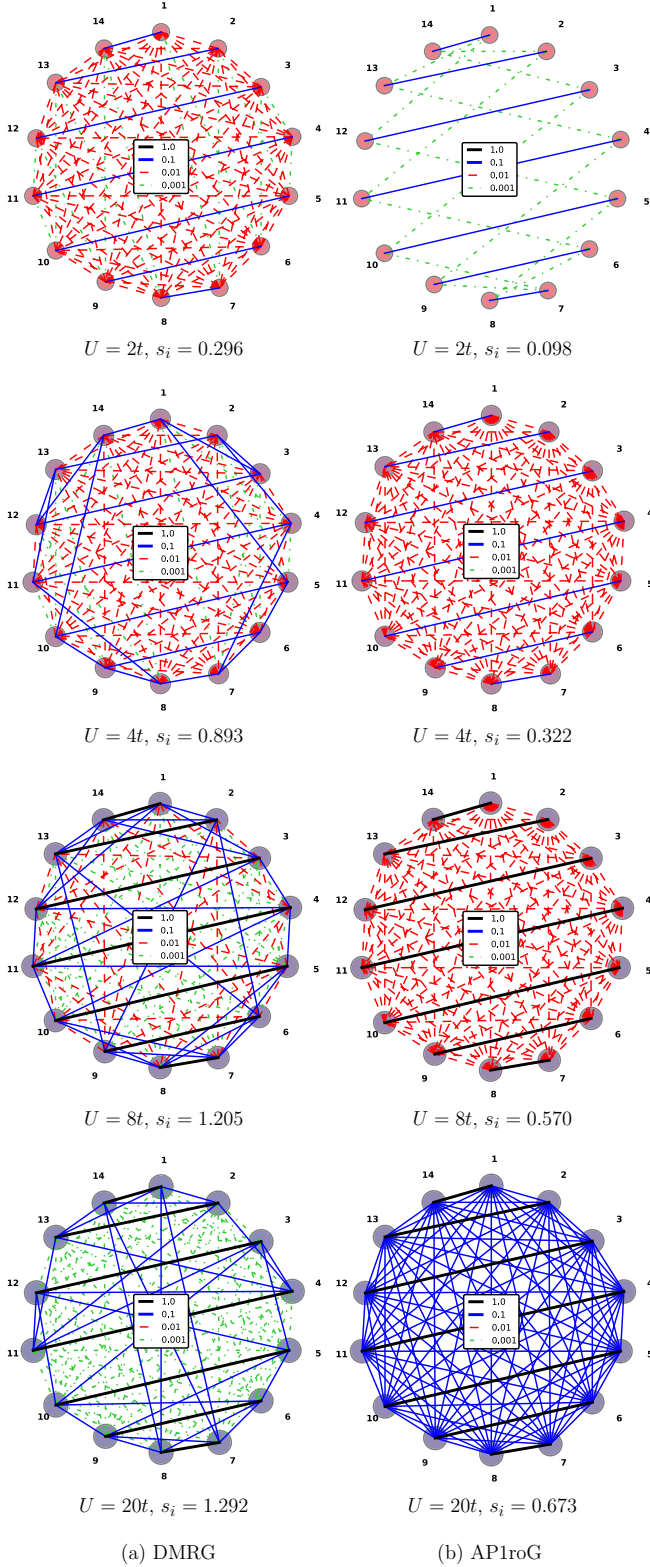


FIG. 1. Orbital-pair mutual information for the half-filled 1D Hubbard model with periodic boundary conditions, 14 sites, and different on-site interaction strengths for the optimized AP1roG basis. The single-orbital entropy is site independent and given below each figure. The strength of the orbital-pair correlations for both the (a) DMRG (left panel) and the (b) AP1roG (right panel) correlation diagrams are color coded: the black lines indicate strong correlations, whereas the green lines indicate weak correlations.

obtained from DMRG and AP1roG calculations. Figure 2(b) shows the spectrum of ρ_i for each site index i . Note that, for AP1roG, ρ_i is a 2×2 matrix, whereas DMRG also includes the spin-up and spin-down contributions and is thus represented by a 4×4 matrix. Furthermore, since we have introduced a reference determinant $|\Phi_0\rangle$ that differs between occupied ($i \in \{1, 2, \dots, 7\}$) and virtual ($i \in \{8, 9, \dots, 14\}$) orbitals, the corresponding site/orbital entropies are not equivalent. This is also evident from Eq. (12), which contains the natural occupation numbers γ_i^i with $\gamma_i^i \approx 2$ for occupied orbitals and $\gamma_i^i \approx 0$ for virtual orbitals, respectively. For small U/t , the eigenvalues $\omega_{\alpha,i}$ are either close to one or close to zero, and the spectrum of ρ_i obtained by AP1roG is qualitatively similar to the DMRG reference. For large U/t , the contributions of $|\uparrow\rangle$ and $|\downarrow\rangle$ to s_i are significant and similar in magnitude to $|\rightarrow\rangle$ and $|\nrightarrow\rangle$. Thus, in the strong correlation limit, the contributions of $|\uparrow\rangle$ and $|\downarrow\rangle$ are important, and the wave function cannot be accurately described by the seniority-zero sector alone, even if the AP1roG basis is optimized.

Similar conclusions can be drawn from the spectrum of $\rho_{i,j}$. Figure 2(c) shows the eigenvalues of $\rho_{i,j}$ for each orbital pair i, j . The eigenvalues for each pair i, j are ordered as in Fig. 2(a). Note that blocks spanned by states that preserve the particle number n and the s_z quantum number are decoupled. Thus, states spanned by $|\rightarrow, \rightarrow\rangle$ and $|\nrightarrow, \nrightarrow\rangle$ represent two (uncoupled) eigenvectors with $(n, s_z) = (0, 0)$ and $(n, s_z) = (4, 0)$, respectively, whereas the states $|\rightarrow, \nrightarrow\rangle$ and $|\nrightarrow, \rightarrow\rangle$ couple to the states $|\uparrow, \uparrow\rangle$ and $|\downarrow, \downarrow\rangle$, which correspond to the sub-block $(n, s_z) = (2, 0)$. The latter basis vectors ($|\uparrow, \uparrow\rangle$ and $|\downarrow, \downarrow\rangle$) always have zero contributions if the wave function is restricted to electron-pair states, and hence, only the $|\rightarrow, \nrightarrow\rangle$ and $|\nrightarrow, \rightarrow\rangle$ sectors are coupled. Due to the coupling between $|\uparrow, \uparrow\rangle$, $|\downarrow, \downarrow\rangle$, $|\rightarrow, \nrightarrow\rangle$, and $|\nrightarrow, \rightarrow\rangle$, we cannot assign an eigenvalue to a specific local state, and the corresponding eigenvalues are marked by the same symbol in Fig. 2(c). We should note, however, that the coupling between the doubly occupied/unoccupied and the singly occupied states is, in general, small and becomes, however, non-negligible for large values of U/t . Furthermore, we will restrict our analysis of $\rho_{i,j}$ to the three sub-blocks $(n, s_z) = \{(0, 0), (2, 0), (4, 0)\}$ spanned by $|\uparrow, \uparrow\rangle$, $|\downarrow, \downarrow\rangle$, $|\rightarrow, \nrightarrow\rangle$, $|\nrightarrow, \rightarrow\rangle$, and $|\uparrow, \downarrow\rangle$ as these sub-blocks (excluding the singly occupied states) are nonzero for the AP1roG wave function. The complete eigenvalue spectrum obtained by DMRG calculations is summarized in the Supplemental Material [76].

As observed for ρ_i , AP1roG reproduces the largest eigenvalues ($\omega_{\alpha,i,j} > 0.01$) for small U/t . For large U/t , the dominant eigenvalues of $\rho_{i,j}$ are overestimated in AP1roG compared to the DMRG reference. Simultaneously, $\omega_{\alpha,i,j}$'s attributed to the singly occupied states increase considerably. As expected, in the strong correlation limit, such singly occupied states become important, especially for the description of weak orbital-pair correlations ($I_{ij} \leq 0.001$). If these singly occupied states are excluded in the wave-function expansion (as in wave functions built from electron-pair states), the spectrum of $\rho_{i,j}$ cannot be properly described. Thus, the two-orbital entropy is underestimated, which, in turn, overvalues the orbital-pair mutual information for small $I_{ij} \leq 0.001$ [cf. Figs. 1 and 2(a)]. We should emphasize that the largest

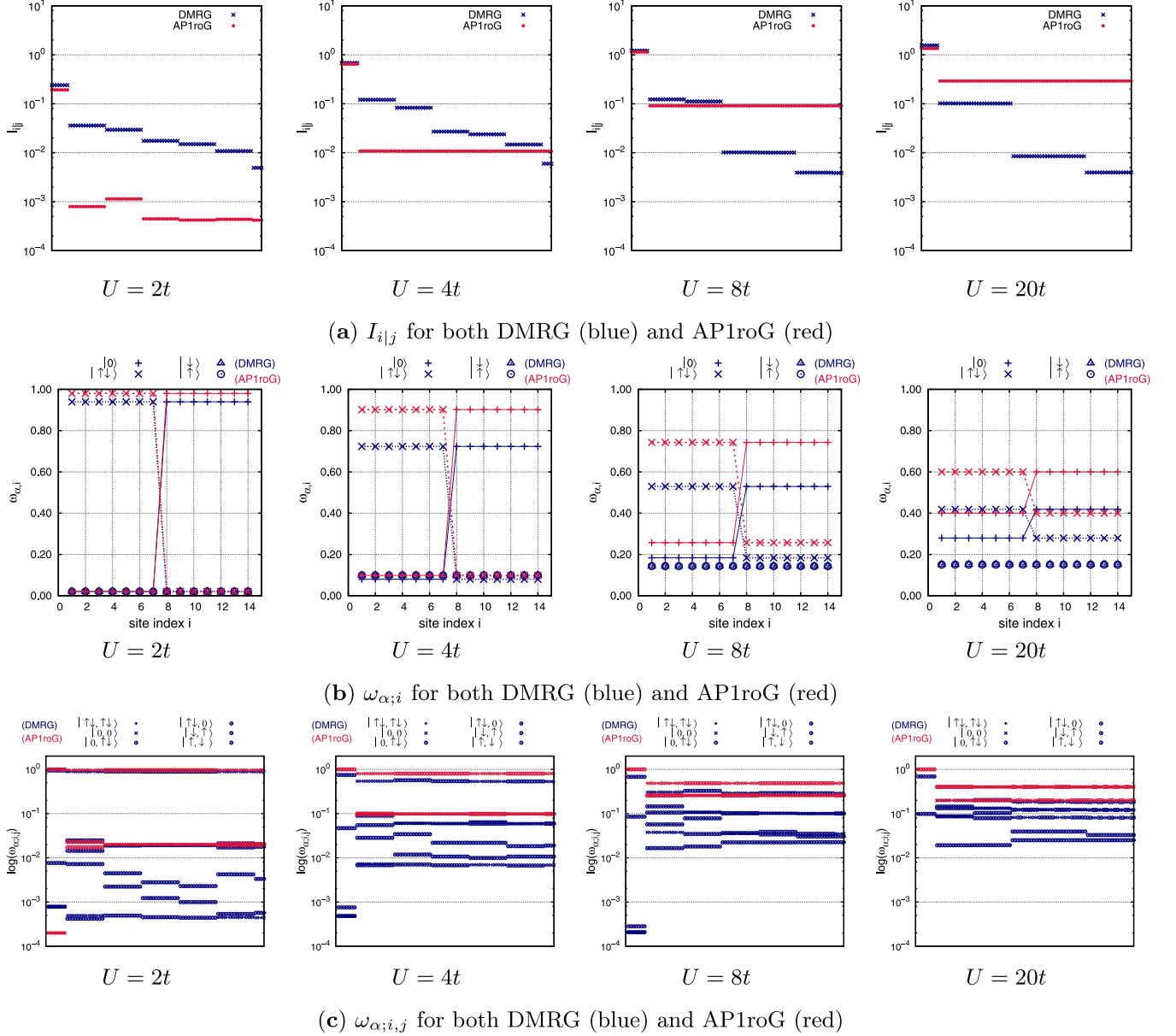


FIG. 2. Decaying values of the mutual information for the half-filled Hubbard model with 14 sites using the optimized AP1roG orbital basis (a). $I_{i|j}$ is sorted with respect to the DMRG reference values so that each value of $I_{i|j}$ is shown for the same orbital pair i and j in both DMRG and AP1roG calculations. Eigenvalues of the (b) one-orbital reduced density matrix and (c) two-orbital reduced density matrix for the half-filled Hubbard model with 14 sites obtained in DMRG and AP1roG calculations using the optimized AP1roG orbital basis. The eigenvalues of $\rho_{i,j}$ for each pair i, j are ordered as in (a). The red lines and symbols indicate AP1roG data, whereas the blue lines and symbols mark the corresponding DMRG results.

orbital-pair correlations are accurately reproduced by AP1roG for large on-site interaction strengths. For these orbital-pair correlations, however, only the eigenvalues of ρ_i contribute to $I_{i|j}$ as $\omega_{\alpha;i,j} \approx 1.0$ (cf. Fig. 2).

Finally, we should note the coupling between doubly occupied/empty and singly occupied states. Whereas for all U/t , the $|\uparrow, \uparrow\rangle/|\downarrow, \uparrow\rangle$ and $|\downarrow, \uparrow\rangle/|\uparrow, \uparrow\rangle$ states are uncoupled for the largest orbital-pair correlations (for instance, indices 1/14, 2/13, etc., in Fig. 1), for intermediate and weak correlations the coupling increases with increasing U/t (see Table I).

IV. DISSOCIATION OF HYDROGEN RINGS

Next, we will shortly comment on the symmetric and asymmetric stretchings of the H_{14} molecule. The symmetrically stretched hydrogen ring will be referred to as metallic H_{14} , whereas the asymmetrically stretched H_{14} ring will be indicated as the molecular hydrogen ring as the dissociation process will result in separated hydrogen molecules [77–80]. Furthermore, in molecular H_{14} , the distance between the hydrogen atoms of the separated hydrogen molecules was kept fixed at 1.41 bohr in accordance with Ref. [77]. For the symmetric and asymmetric dissociations of H_{14} , the quantum

TABLE I. Selected eigenvalues and eigenvectors of $\rho_{i,j}$ for selected orbital pairs of the one-dimensional Hubbard model with 14 sites and different on-site interaction strengths. Only the largest of the four eigenvectors of the $(n, s_z) = (2, 0)$ sub-block are shown.

(i, j)	U/t	$\omega_{\alpha,i,j}$	$(n, s_z) = (2, 0)$			
			$ \downarrow, \uparrow\rangle$	$ \uparrow, \downarrow\rangle$	$ \downarrow, \downarrow\rangle$	$ \uparrow, \uparrow\rangle$
1, 2	2	0.025	0.690	0.690	-0.155	0.155
	4	0.064	0.683	0.683	-0.184	0.184
	8	0.146	-0.571	-0.571	-0.418	0.418
	20	0.145	0.636	0.636	0.308	-0.308
1, 13	2	0.005	-0.052	0.040	-0.706	0.706
	4	0.022	-0.141	0.088	-0.697	0.697
	8	0.078	0.301	-0.219	-0.656	0.656
	20	0.103	-0.635	0.169	0.533	-0.533

system is described by the nonrelativistic quantum chemical Hamiltonian, which reads in its second quantized form

$$\hat{H} = \sum_{pq,\sigma} h_{pq} a_{p\sigma}^\dagger a_{q\sigma} + \frac{1}{2} \sum_{pqrs,\sigma\tau} \langle pq|rs \rangle a_{p\sigma}^\dagger a_{q\tau}^\dagger a_{s\tau} a_{r\sigma} + H_{\text{nuc}}, \quad (17)$$

where the first term contains both the kinetic energy and the nuclear-electron attraction, the second term represents the repulsive electron-electron interaction, and the third term is the nuclear-nuclear repulsion energy, respectively. The indices p, q, r , and s run over all one-particle basis functions. By changing the distances between H atoms and H₂ molecules in hydrogen rings, we simulate the one-dimensional Hubbard (metallic H₁₄) and dimerized Hubbard model (molecular H₁₄) as a function of the on-site interaction U using an *ab initio* treatment. As for the Hubbard model, the final basis states used in our numerical calculations do not correspond to an on-site localized basis. Due to the similarities to the one-dimensional Hubbard model and dimerized Hubbard model, we will not discuss the orbital-pair correlations in detail. Instead, we will briefly comment on the influence of the optimization of the basis functions on orbital-pair correlations and the eigenvalue spectra of the orbital reduced density matrices. A thorough analysis of hydrogen rings, including the total electronic energies and potential-energy surfaces obtained by DMRG and AP1roG, can be found in the Supplemental Material [76].

The influence of orbital optimization on orbital-pair correlations in H₁₄

We will compare the orbital correlation and entanglement diagrams obtained by DMRG and AP1roG in the canonical Hartree-Fock basis to those calculated in the natural orbital basis optimized within the AP1roG model and the STO-6G basis set. For all investigated systems, AP1roG misses a substantial amount of (static and dynamic) orbital-pair correlations and orbital entanglement. However, within the canonical Hartree-Fock basis, AP1roG captures a larger fraction of the weaker orbital-pair correlations (with $I_{i|j} < 10^{-2}$) than using the optimized natural AP1roG orbitals (see Fig. S9 in the Supplemental Material [76]). Furthermore, all orbital-pair correlations predicted by AP1roG (in the Hartree-Fock basis) are smaller than the DMRG reference values, which

indicates that overcorrelation does not occur when canonical Hartree-Fock orbitals are used to construct the geminals. These observations are confirmed by the decay of the orbital-pair mutual information displayed in Supplemental Material Fig. S6 [76] [for increasing interatomic H-H distances, we always have $I_{i|j}(\text{AP1roG}) < I_{i|j}(\text{DMRG})$]. Despite underestimating a large fraction of the orbital-pair correlations, the decay of $I_{i|j}(\text{AP1roG})$ qualitatively agrees with the DMRG reference distribution for all investigated points along the dissociation pathway. This is not the case if the orbitals are optimized within the AP1roG method where AP1roG does not predict a stepped decay of $I_{i|j}$ as obtained in DMRG calculations.

A similar observation can be made for the eigenvalues of ρ_i and $\rho_{i,j}$. Specifically, optimization of the orbital basis within the AP1roG model reduces the contributions of $\omega_{\uparrow,i}$ and $\omega_{\downarrow,i}$ to the spectrum of ρ_i . Although AP1roG (in the Hartree-Fock basis) can accurately reproduce the dominant part of the spectrum of ρ_i and $\rho_{i,j}$ for squeezed hydrogen rings and around the equilibrium geometry, it fails, however, for stretched hydrogen rings where the eigenvalues are substantially over- or underestimated.

Finally, we would like to comment on the influence of the size of the atomic orbital basis on orbital-pair correlations and orbital entanglement. We have performed additional calculations for metallic and molecular H₁₄ rings using the correlation-consistent basis set of double- ζ quality (cc-pVDZ [81]) and stretched molecular geometries. Most importantly, the overestimation of strong and intermediate orbital-pair correlations is not caused by the small basis set size used in our calculations. Although increasing the atomic basis set to cc-pVDZ quality reduces the extent of overcorrelation, it does not completely eliminate the failures of AP1roG to provide reliable spectra of ρ_i and $\rho_{i,j}$. To remedy this problem, open-shell configurations have to be included in the wave-function model. The corresponding correlation diagrams are summarized in the Supplemental Material [76].

V. CONCLUSIONS

Wave functions constructed from electron-pair states, that is, so-called seniority-zero wave functions, are considered good models to describe strongly correlated systems in condensed-matter physics and quantum chemistry. However, most of the analysis presented so far was mainly based on energetic arguments or on evaluation of one-body correlation

functions, such as occupation numbers. In this paper, we have presented an in-depth analysis of the correlations between the one-particle functions that are used to construct the geminals. Specifically, we have scrutinized how accurately the AP1roG model can reproduce orbital-pair correlations and orbital entanglement in the one-dimensional Hubbard model with periodic boundary conditions as well as in metallic and molecular hydrogen rings.

If the orbitals, and thus the reference determinant, are optimized, AP1roG can accurately describe the largest orbital-pair correlations in all investigated systems and misses, however, a large fraction of the weaker orbital-pair correlations. In the strong correlation limit, AP1roG considerably overestimates intermediate and weaker orbital-pair correlations and results in a prolonged plateau of the mutual information. This overcorrelation can be explained by the eigenvalue spectra of ρ_i (one-orbital reduced density matrix) and $\rho_{i,j}$ (two-orbital reduced density matrix), which are used to determine the orbital-based correlation functions. Whereas in the weak correlation limit, the eigenvalues corresponding to singly occupied states are (orders of magnitudes) smaller than those corresponding to doubly occupied or empty states, their weights gradually increase when we approach the strong correlation regime. Specifically, in the strong correlation limit, singly occupied states become important and need to be included in the wave-function model to accurately describe the spectra of ρ_i and $\rho_{i,j}$, even if the orbital basis is optimized. It remains, however, ambiguous if the AP1roG model provides an accurate zero-order wave function (in the strong correlation limit) and if *a posteriori* models, such as perturbation theory or coupled-cluster-type corrections, provide enough flexibility

to correct the (zero-order) orbital-pair correlations. This is currently under investigation in our laboratory.

If the one-particle functions are not optimized and the Hartree-Fock determinant is taken as a reference determinant in the AP1roG ansatz, all orbital-pair correlations are smaller than the DMRG reference values. Thus, overcorrelation is introduced through the optimization of the AP1roG basis, which minimizes the total electronic energy but simultaneously deteriorates orbital-pair correlations. Finally, we should note that, for molecular geometries around the equilibrium structure, both the $I_{i|j}$ and the eigenvalue spectra of ρ_i and $\rho_{i,j}$ suggest that AP1roG provides accurate zero-order wave functions (with and without orbital optimization) where the missing orbital-pair correlations could be accurately modeled using *a posteriori* approaches for weak electron correlation [75,82–85]. A detailed analysis of orbital-pair correlations predicted by *a posteriori* correlation models will be the subject of future publications.

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- [1] J. Dukelsky, S. Pittel, and G. Sierra, *Rev. Mod. Phys.* **76**, 643 (2004).
 - [2] J. Hubbard, *Proc. R. Soc. London, Ser. A* **276**, 238 (1963).
 - [3] E. H. Lieb and F. Y. Wu, *Phys. Rev. Lett.* **20**, 1445 (1968).
 - [4] J. P. F. LeBlanc, A. E. Antipov, F. Becca, I. W. Bulik, G. K.-L. Chan, C.-M. Chung, Y. Deng, M. Ferrero, T. M. Henderson, C. A. Jiménez-Hoyos, E. Kozik, X.-W. Liu, A. J. Millis, N. V. Prokof'ev, M. Qin, G. E. Scuseria, H. Shi, B. V. Svistunov, L. F. Tocchio, I. S. Tupitsyn, S. R. White, S. Zhang, B.-X. Zheng, Z. Zhu, and E. Gull (Simons Collaboration on the Many-Electron Problem) *Phys. Rev. X* **5**, 041041 (2015).
 - [5] S. R. White, *Phys. Rev. Lett.* **69**, 2863 (1992).
 - [6] S. R. White, *Phys. Rev. B* **48**, 10345 (1993).
 - [7] S. R. White and R. L. Martin, *J. Chem. Phys.* **110**, 4127 (1999).
 - [8] U. Schollwöck, *Rev. Mod. Phys.* **77**, 259 (2005).
 - [9] O. Legeza, R. M. Noack, J. Sólyom, and L. Tincani, in *Computational Many-Particle Physics*, Lecture Notes in Physics, edited by H. Fehske, R. Schneider, and A. Weiße, Vol. 739 (Springer, Berlin/Heidelberg, 2008), pp. 653–664.
 - [10] K. H. Marti and M. Reiher, *Z. Phys. Chem.* **224**, 583 (2010).
 - [11] G. K.-L. Chan and S. Sharma, *Annu. Rev. Phys. Chem.* **62**, 465 (2011).
 - [12] S. Wouters and D. Van Neck, *Eur. Phys. J. D* **68**, 272 (2014).
 - [13] S. Szalay, M. Pfeiffer, V. Murg, G. Barcza, F. Verstraete, R. Schneider, and Ö. Legeza, *Int. J. Quantum Chem.* **115**, 1342 (2015).
 - [14] T. Yanai, Y. Kurashige, W. Mizukami, J. Chalupsky, T. N. Lan, and M. Saitow, *Int. J. Quantum Chem.* **115**, 283 (2015).
 - [15] G. Ehlers, J. Sólyom, O. Legeza, and R. M. Noack, *Phys. Rev. B* **92**, 235116 (2015).
 - [16] S. Zhang, *Emergent Phenomena in Correlated Matter: Autumn School Organized by the Forschungszentrum Jülich and the German Research School for Simulation Sciences*, Forschungszentrum Jülich, 2013, edited by E. Pavarini, E. Koch, and U. Schollwöck (Forschungszentrum Jülich GmbH Institute for Advanced Simulation, Jülich, Germany, 2013), Vol. 3.
 - [17] S. Hochkeppel, T. C. Lang, C. Brünger, F. F. Assaad, and W. Hanke, *High Performance Computing in Science and Engineering, Garching/Munich 2007* (Springer, Berlin/Heidelberg, 2008), pp. 669–686.
 - [18] L. Stella, C. Attaccalite, S. Sorella, and A. Rubio, *Phys. Rev. B* **84**, 245117 (2011).
 - [19] A. C. Hurley, J. Lennard-Jones, and J. A. Pople, *Proc. R. Soc. London, Ser. A* **220**, 446 (1953).
 - [20] A. J. Coleman, *J. Math. Phys.* **6**, 1425 (1965).
 - [21] D. M. Silver, *J. Chem. Phys.* **50**, 5108 (1969).
 - [22] J. V. Ortiz, B. Weiner, and Y. Öhrn, *Int. J. Quantum Chem.* **20**, 113 (1981).
 - [23] P. R. Surjan, *Correlation and Localization* (Springer, Heidelberg, 1999), pp. 63–88.
 - [24] W. Kutzelnigg, *Chem. Phys.* **401**, 119 (2012).

- [25] P. R. Surján, A. Szabados, P. Jeszenszki, and T. Zoboki, *J. Math. Chem.* **50**, 534 (2012).
- [26] J. K. Ellis, R. L. Martin, and G. E. Scuseria, *J. Chem. Theory Comput.* **9**, 2857 (2013).
- [27] P. A. Limacher, P. W. Ayers, P. A. Johnson, S. De Baerdemacker, D. Van Neck, and P. Bultinck, *J. Chem. Theory Comput.* **9**, 1394 (2013).
- [28] R. G. Parr, F. O. Ellison, and P. G. Lykos, *J. Chem. Phys.* **24**, 1106 (1956).
- [29] J. M. Parks and R. G. Parr, *J. Chem. Phys.* **28**, 335 (1958).
- [30] W. Kutzelnigg, *J. Chem. Phys.* **40**, 3640 (1964).
- [31] W. Kutzelnigg, *Theoret. Chim. Acta* **3**, 241 (1965).
- [32] V. A. Rassolov, *J. Chem. Phys.* **117**, 5978 (2002).
- [33] K. Pernal, *J. Chem. Theory Comput.* **10**, 4332 (2014).
- [34] A. J. Coleman, *Int. J. Quantum Chem.* **63**, 23 (1997).
- [35] E. Neuscamman, *Phys. Rev. Lett.* **109**, 203001 (2012).
- [36] E. Neuscamman, *J. Chem. Theory Comput.* **12**, 3149 (2016).
- [37] C. A. Jiménez-Hoyos, T. M. Henderson, T. Tsuchimochi, and G. E. Scuseria, *J. Chem. Phys.* **136**, 164109 (2012).
- [38] S. Bratoz and P. Durand, *J. Chem. Phys.* **43**, 2670 (1965).
- [39] D. M. Silver, *J. Chem. Phys.* **52**, 299 (1970).
- [40] G. Náray-Szabó, *J. Chem. Phys.* **58**, 1775 (1973).
- [41] G. Náray-Szabó, *Int. J. Quantum Chem.* **9**, 9 (1975).
- [42] E. Rosta and P. R. Surján, *J. Chem. Phys.* **116**, 878 (2002).
- [43] K. Boguslawski, P. Tecmer, P. W. Ayers, P. Bultinck, S. De Baerdemacker, and D. Van Neck, *Phys. Rev. B* **89**, 201106(R) (2014).
- [44] F. Weinhold and E. B. Wilson, *J. Chem. Phys.* **46**, 2752 (1967).
- [45] T. M. Henderson, G. E. Scuseria, J. Dukelsky, A. Signoracci, and T. Duguet, *Phys. Rev. C* **89**, 054305 (2014).
- [46] T. Stein, T. M. Henderson, and G. E. Scuseria, *J. Chem. Phys.* **140**, 214113 (2014).
- [47] T. M. Henderson, I. W. Bulik, and G. E. Scuseria, *J. Chem. Phys.* **142**, 214116 (2015).
- [48] P. Tecmer, K. Boguslawski, P. A. Limacher, P. A. Johnson, M. Chan, T. Verstraeten, and P. W. Ayers, *J. Phys. Chem. A* **118**, 9058 (2014).
- [49] K. Boguslawski, P. Tecmer, P. A. Limacher, P. A. Johnson, P. W. Ayers, P. Bultinck, S. De Baerdemacker, and D. Van Neck, *J. Chem. Phys.* **140**, 214114 (2014).
- [50] P. A. Limacher, T. D. Kim, P. W. Ayers, P. A. Johnson, S. De Baerdemacker, D. Van Neck, and P. Bultinck, *Mol. Phys.* **112**, 853 (2014).
- [51] K. Boguslawski, P. Tecmer, P. W. Ayers, P. Bultinck, S. De Baerdemacker, and D. Van Neck, *J. Chem. Theory Comput.* **10**, 4873 (2014).
- [52] P. Tecmer, K. Boguslawski, and P. W. Ayers, *Phys. Chem. Chem. Phys.* **17**, 14427 (2015).
- [53] P. A. Limacher, *J. Chem. Theory Comput.* **11**, 3629 (2015).
- [54] J. Rissler, R. M. Noack, and S. R. White, *Chem. Phys.* **323**, 519 (2006).
- [55] G. Barcza, O. Legeza, K. H. Marti, and M. Reiher, *Phys. Rev. A* **83**, 012508 (2011).
- [56] O. Legeza, G. Barcza, R. M. Noack, and J. Sólyom, Entanglement Patterns in Strongly Correlated Systems, Dresden, Germany, 2013 (unpublished).
- [57] K. Boguslawski, P. Tecmer, O. Legeza, and M. Reiher, *J. Phys. Chem. Lett.* **3**, 3129 (2012).
- [58] K. Boguslawski, P. Tecmer, G. Barcza, O. Legeza, and M. Reiher, *J. Chem. Theory Comput.* **9**, 2959 (2013).
- [59] K. Boguslawski and P. Tecmer, *Int. J. Quantum Chem.* **115**, 1289 (2015).
- [60] G. Barcza, R. M. Noack, J. Sólyom, and Ö. Legeza, *Phys. Rev. B* **92**, 125140 (2015).
- [61] M. Mottet, P. Tecmer, K. Boguslawski, O. Legeza, and M. Reiher, *Phys. Chem. Chem. Phys.* **16**, 8872 (2014).
- [62] T. Szilvási, G. Barcza, and Ö. Legeza, *arXiv:1509.04241* (2015).
- [63] K. Boguslawski and M. Reiher, *The Chemical Bond: Chemical Bonding Across the Periodic Table*, edited by G. Frenking and S. Shaik (Wiley, Hoboken, NJ, 2014), pp. 219–252.
- [64] L. Freitag, S. Knecht, S. F. Keller, M. G. Delcey, F. Aquilante, T. B. Pedersen, R. Lindh, M. Reiher, and L. Gonzalez, *Phys. Chem. Chem. Phys.* **17**, 13769 (2015).
- [65] Y. Zhao, K. Boguslawski, P. Tecmer, C. Duperrouzel, G. Barcza, Ö. Legeza, and P. W. Ayers, *Theor. Chem. Acc.* **134**, 120 (2015).
- [66] V. Murg, F. Verstraete, R. Schneider, P. R. Nagy, and Ö. Legeza, *J. Chem. Theory Comput.* **11**, 1027 (2015).
- [67] E. Fertitta, B. Paulus, G. Barcza, and Ö. Legeza, *Phys. Rev. B* **90**, 245129 (2014).
- [68] C. Duperrouzel, P. Tecmer, K. Boguslawski, G. Barcza, O. Legeza, and P. W. Ayers, *Chem. Phys. Lett.* **621**, 160 (2015).
- [69] S. Keller, K. Boguslawski, T. Janowski, M. Reiher, and P. Pulay, *J. Chem. Phys.* **142**, 244104 (2015).
- [70] C. J. Stein and M. Reiher, *J. Chem. Theory Comput.* **12**, 1760 (2016).
- [71] K. Boguslawski, F. Réal, P. Tecmer, C. Duperrouzel, A. S. P. Gomes, Ö. Legeza, P. W. Ayers, and V. Vallet, *arXiv:1608.02353* (2016).
- [72] Ö. Legeza and J. Sólyom, *Phys. Rev. B* **68**, 195116 (2003).
- [73] Ö. Legeza and J. Sólyom, *Phys. Rev. Lett.* **96**, 116401 (2006).
- [74] E. A. Salter, G. W. Trucks, and R. J. Bartlett, *J. Chem. Phys.* **90**, 1752 (1989).
- [75] T. M. Henderson, I. W. Bulik, T. Stein, and G. E. Scuseria, *J. Chem. Phys.* **141**, 244104 (2014).
- [76] See Supplemental Material at <http://link.aps.org/supplemental/10.1103/PhysRevB.94.155126> for DMRG and AP1roG ground-state energies, additional correlation functions, and eigenvalue spectra of the one- and two-orbital reduced density matrices for the half-filled one-dimensional Hubbard model and hydrogen rings. Thorough analysis of orbital-pair correlations in hydrogen rings.
- [77] M. Seel, P. S. Bagus, and J. Ladik, *J. Chem. Phys.* **77**, 3123 (1982).
- [78] C.-M. Liegener and J. Ladik, *Phys. Lett. A* **107**, 79 (1985).
- [79] J.-M. Anndre, J. Delhalle, J. G. Fripiat, G. Hennico, J.-L. Calais, and L. Piela, *J. Mol. Struct. (Theochem)* **179**, 393 (1988).
- [80] J. S. Wright and G. A. DiLabio, *J. Phys. Chem* **96**, 10793 (1992).
- [81] T. H. Dunning, *J. Chem. Phys.* **90**, 1007 (1989).
- [82] P. Limacher, P. Ayers, P. Johnson, S. De Baerdemacker, D. Van Neck, and P. Bultinck, *Phys. Chem. Chem. Phys.* **16**, 5061 (2014).
- [83] K. Boguslawski and P. W. Ayers, *J. Chem. Theory Comput.* **11**, 5252 (2015).
- [84] A. J. Garza, I. W. Bulik, T. M. Henderson, and G. E. Scuseria, *Phys. Chem. Chem. Phys.* **17**, 22412 (2015).
- [85] A. J. Garza, I. W. Bulik, T. M. Henderson, and G. E. Scuseria, *J. Chem. Phys.* **142**, 044109 (2015).