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ABSTRACT

This work deals with the variational determination of the two-particle reduced density matrix (2-RDM) and the energy corresponding to the ground state of *N*-particle systems within the doubly occupied configuration interaction (DOCI) space. Here, we impose for the first time up to four-particle *N*-representability constraint conditions in the variational determination of the 2-RDM matrix elements using the standard semidefinite programming algorithms. The energies and 2-RDMs obtained from this treatment and the corresponding computational costs are compared with those arisen from previously reported less restrictive variational methods [D. R. Alcoba *et al.*, J. Chem. Phys. **149**, 194105 (2018)] as well as with the exact DOCI values. We apply the different approximations to the one-dimensional XXZ model of quantum magnetism, which has a rich phase diagram with one critical phase and constitutes a stringent test for the method. The numerical results show the usefulness of our treatment to achieve a high degree of accuracy.

I. INTRODUCTION

The description of properties in pairwise interacting *N*-particle systems by means of two-particle reduced density matrices (2-RDMs)[1,2] avoids the high computational cost required to solve the Schrödinger three-dimensional partial differential equation, what is known as the exponential wall problem.[3] Consequently, a great effort has been dedicated, during the last decades, to study the features of these devices, and a great variety of attempts have been proposed to determine exactly the matrix elements of the reduced density matrices.[4–12] The expectation value of any one- or two-particle operator, corresponding to an *N*-particle state, can

straightforwardly be calculated from its 2-RDM without using the N-particle wave function. Compared to the wave function, the 2-RDM is a much more compact object as its matrix dimension scales as L^2, with L being the dimension of the single-particle basis set. In principle, the N-particle system ground state energy could be determined by a simple variational 2-RDM (v2RDM) procedure. However, this direct method does not lead to satisfactory results because it does not assure that the calculated 2-RDM arises from a true N-particle wave function; this is called N-representability problem. An improvement of this direct technique consists in imposing additional constraint conditions so that the resulting 2-RDM approximates to a derivable one from an N-particle wave function as best as possible. The necessary and sufficient N-representability conditions for the 2-RDM are known, but they are of no practical use.[13–16] Consequently, one has to search for a set of necessary but not (in general) sufficient conditions to enforce that the 2-RDM turns out to be N-representable. The most commonly used constraint conditions are the p-particle N-representability ones, known as the p-positivity conditions, which derive from a class of positive semidefinite Hamiltonians; they express the fact that the expectation value of any of these Hamiltonians for any wave function should be nonnegative. The resulting constrained optimization problem is known as a semidefinite program (SDP) which is a well-known class of convex optimization problems for which many general purpose solvers exist.

Unfortunately, on the whole, the v2RDM technique is not computationally competitive with other standard methods employed in many-body theory. Very recently, the 2-RDM variational optimization has been restricted to the doubly occupied configuration interaction (DOCI) space, henceforth called v2RDM-DOCI. This scheme attempts to approximate the 2-RDM to a two-particle matrix arising from a DOCI wave function, that is, an N-particle wave function expanded on N-electron doubly occupied Slater determinants or, equivalently, a wave function belonging to the Hilbert subspace of seniority zero, where the seniority quantum number counts the number of unpaired particles.[17–19] The DOCI wave functions have proven to capture suitably the bulk of the static correlation[20,21] and at the same time present a very sparse structure of the 2-RDM[22] causing the associated semidefinite program to have a very favorable scaling. In the v2RDM-DOCI procedure, a new set of necessary constraints has been added to the standard N-representability conditions so that the 2-RDM obtained turns out to arise from a DOCI wave function. Several applications of the v2RDM-DOCI were implemented and tested against accurate solutions, showing that the lower bounds on the ground-state energies obtained from v2RDM-DOCI calculations converge rapidly with the order of p-positivity.[22–27] In this work, the constraint level has been extended up to four-positivity conditions.

The seniority-zero nature of the DOCI space selects the seniority-zero part of the Hamiltonian which can be expressed in terms of SU(2) spin operators or, equivalently, in terms of hard-core bosons. An important class of SU(2) Hamiltonians are those encompassing the area of quantum magnetism. The formalism developed and tested could directly be applied to the study of spin model systems. Due to the nonperturbative nature of the v2RDM method, it might be possible to describe with high accuracy exotic phases and quantum phase transitions. Here, we will focus our attention on the exactly solvable one dimensional Heisenberg XXZ spin model. The model has a critical antiferromagnetic phase in the thermodynamic limit and two quantum phase transitions which are softened for finite systems, but it still represents an important challenge for any many-body approximation. Minimization of the energy with respect to a 2-RDM is performed constraining the reduced density matrix by a complete set of four-positivity N-representability conditions comprising five types of four-particle probability distributions in the DOCI space. To our knowledge, these conditions have not been derived and implemented so far. We report numerical calculations using the semidefinite programming algorithm described in Refs. 28 and 29 for the ground-state energies and 2-RDMs in the DOCI space across a full range of the Heisenberg model parameters. These results have been compared with those arising from exact numerical calculations, showing that the employed four-positivity conditions provide a significant improvement upon those obtained using only two- and three-positivity conditions, at an affordable increase in computational cost.

This work is organized as follows. In Sec. II, we review the foundations of the variational reduced density matrix theory and the p-positivity N-representability conditions, focusing the attention on the DOCI space. In that section, we also introduce the complete set of four-positivity conditions in that space. In Sec. III, we present the first application of our theory to the Heisenberg XXZ spin model. Finally, in Sec. IV, we summarize the main conclusions of this work.

II. THEORY

The variational reduced density matrix theory and its formulation in the DOCI space are discussed in Secs. II A and II B, respectively.

A. Variational reduced density matrix theory

In second quantization, the Hamiltonian of an N-particle pairwise interacting system can be written as[30]

$$H = \sum_{ij} t_{ij}\, a_i^\dagger a_j + \frac{1}{4} \sum_{ijkl} V_{ijkl}\, a_i^\dagger a_j^\dagger a_l a_k, \tag{1}$$

where t_{ij} and V_{ijkl} are the one-body energy and the two-body interaction terms, respectively, and $a_i^\dagger$ and a_j are the standard fermion creation and annihilation operators in a given finite orthonormal single-particle basis $\{i, j, k, l, \ldots\}$.

According to Eq. (1), the energy of the ground state $|\psi\rangle$ of the N-particle system, E_0, can be expressed as[31–33]

$$E_0 = \frac{1}{4} \sum_{ijkl} \left[\frac{1}{N-1} \left(t_{ik}\delta_{jl} - t_{jk}\delta_{il} - t_{il}\delta_{jk} + t_{jl}\delta_{ik} \right) + V_{ijkl} \right] {}^2D_{ijkl}, \tag{2}$$

where

$${}^2D_{ijkl} = \langle \psi | a_i^\dagger a_j^\dagger a_l a_k | \psi \rangle \tag{3}$$

is the two-particle reduced density matrix. In principle, this equation indicates that the ground-state energy of the system may be computed by direct variation of the matrix ${}^2D$. However, this is not

the case because not every calculated ${}^2D$ derives from the integration of an N-particle wave function.[1,34] This difficulty leads to the well-known N-representability problem which aims to define a set of necessary and sufficient conditions ensuring that a reduced density matrix stems from an N-particle physical system. In general, the reduced density matrices must be hermitian, properly normalized, and be related by contraction mappings. Additionally, a hierarchy of necessary, albeit not sufficient, set of constraints on the p-RDM constitutes the p-positivity N-representability conditions.[35,36] These conditions derive from the positive semidefinite property of a class of Hamiltonians of the form

$$H = B^\dagger B, \tag{4}$$

where $B^\dagger$ is a p-particle operator. The expectation value of this Hamiltonian must be non-negative. Therefore, its matrix representation must be positive semidefinite. Different forms of this operator lead to different p-positivity conditions. In the two-particle space, these yield the well-known 2-$\mathcal{P}$, 2-$\mathcal{Q}$, and 2-$\mathcal{G}$ two-positivity conditions,[13,34] which require the positive semidefiniteness of the two-particle, two-hole, and particle-hole representations of the 2-RDM,

$${}^2D_{ijnm} = \langle\psi|a_i^\dagger a_j^\dagger a_m a_n|\psi\rangle \geq 0, \tag{5a}$$

$${}^2Q_{ijnm} = \langle\psi|a_i a_j a_m^\dagger a_n^\dagger|\psi\rangle \geq 0, \tag{5b}$$

$${}^2G_{ijnm} = \langle\psi|a_i^\dagger a_j a_m^\dagger a_n|\psi\rangle \geq 0, \tag{5c}$$

respectively. Even though these three representations can be related to each other, restricting any of them to be positive semidefinite does not imply the positivity of the other two. Therefore, each of the two-positivity conditions provides distinct N-representability constraints of the 2-RDM. Analogously to the two-positivity conditions, the 3-$\mathcal{P}$, 3-$\mathcal{Q}$, 3-$\mathcal{E}$, and 3-$\mathcal{F}$ three-positivity conditions[23,26,37–41] and the 4-$\mathcal{P}$, 4-$\mathcal{Q}$, 4-$\mathcal{E}$, 4-$\mathcal{F}$, and 4-$\mathcal{G}$ four-positivity conditions[36] require the positive semidefiniteness of the four and the five representations of the 3-RDM and 4-RDM,

$${}^3D_{ijkonm} = \langle\psi|a_i^\dagger a_j^\dagger a_k^\dagger a_m a_n a_o|\psi\rangle \geq 0, \tag{6a}$$

$${}^3Q_{ijkonm} = \langle\psi|a_i a_j a_k a_m^\dagger a_n^\dagger a_o^\dagger|\psi\rangle \geq 0, \tag{6b}$$

$${}^3E_{ijkonm} = \langle\psi|a_i^\dagger a_j^\dagger a_k a_m^\dagger a_n a_o|\psi\rangle \geq 0, \tag{6c}$$

$${}^3F_{ijkonm} = \langle\psi|a_i^\dagger a_j a_k a_m^\dagger a_n^\dagger a_o|\psi\rangle \geq 0, \tag{6d}$$

and

$${}^4D_{ijklponm} = \langle\psi|a_i^\dagger a_j^\dagger a_k^\dagger a_l^\dagger a_m a_n a_o a_p|\psi\rangle \geq 0, \tag{7a}$$

$${}^4Q_{ijklponm} = \langle\psi|a_i a_j a_k a_l a_m^\dagger a_n^\dagger a_o^\dagger a_p^\dagger|\psi\rangle \geq 0, \tag{7b}$$

$${}^4E_{ijklponm} = \langle\psi|a_i^\dagger a_j^\dagger a_k^\dagger a_l a_m^\dagger a_n a_o a_p|\psi\rangle \geq 0, \tag{7c}$$

$${}^4F_{ijklponm} = \langle\psi|a_i^\dagger a_j a_k a_l a_m^\dagger a_n^\dagger a_o^\dagger a_p|\psi\rangle \geq 0, \tag{7d}$$

$${}^4G_{ijklponm} = \langle\psi|a_i^\dagger a_j^\dagger a_k a_l a_m^\dagger a_n^\dagger a_o a_p|\psi\rangle \geq 0, \tag{7e}$$

respectively. These conditions provide distinct constraints on the N-representability of the 3-RDM and 4-RDM and, by contraction, of the 2-RDM. Although these conditions were previously considered by several authors,[36] and they were shown to provide very accurate energies and 2-RDMs, the scaling of its computational implementation severely limits its applicability to very small systems. In particular, for the three- and four-positivity conditions, the basic matrix operations entering the calculations exhibit a prohibitive scaling of $O(L^9)$ and $O(L^{12})$, respectively.

B. Variational reduced density matrix theory in the DOCI space

Recently, the v2RDM approach has been applied within the restricted DOCI space, notably reducing its computational scaling. The method is adequate for studying Hamiltonians with interactions in the DOCI space, i.e., interactions that do not change the number of paired particles. For this class of Hamiltonians, the seniority number, which classifies the Hilbert space into subspaces with a given number of singly occupied levels,[42] is also an exact quantum number, as unpaired particles do not interact with the rest of the system since seniority-zero Hamiltonians do not allow for pair breaking.

The most general Hamiltonian within the seniority-zero subspace can be written as

$$H = \sum_i \epsilon_i n_i + \sum_{i\neq j} w_{ij} n_i n_j + \sum_{ij} v_{ij} b_i^\dagger b_j\,, \tag{8}$$

where ϵ_i are the energies of L doubly degenerate fermion single-particle levels and w_{ij} and v_{ij} stand for the monopole and pairing interactions, respectively. The operators $b_i^\dagger$ and $(2n_i - 1)/2$ are the generators of the SU(2) pair algebra, satisfying the following hard-core bosons relations:

$$[b_i, b_j^\dagger] = \delta_{ij}(1 - 2n_i), \quad (b_i^\dagger)^2 = 0. \tag{9}$$

These operators are related to the fermion creation and annihilation operators as follows: $n_i = \frac{1}{2}(a_i^\dagger a_i + a_{\bar{i}}^\dagger a_{\bar{i}})$ and $b_i^\dagger = (b_i)^\dagger = a_i^\dagger a_{\bar{i}}^\dagger$. The $(i, \bar{i})$ pair defines the fermion pairing scheme, which can involve two particles with either opposite spins $(i\uparrow, i\downarrow)$, momenta $(i, -i)$, or in general any classification of conjugate quantum numbers in doubly degenerate single-particle levels. The ground-state energy of Hamiltonian (8) can then be cast as[23,37,38]

$$E_0 = \sum_{ij} J_{ij}\Pi_{ij} + \sum_{i\neq j} w_{ij} D_{ij}, \tag{10}$$

where

$$J_{ij} = \delta_{ij}\epsilon_i + v_{ij}. \tag{11}$$

The Π and D matrices given by

$$\Pi_{ij} = \langle\psi|b_i^\dagger b_j|\psi\rangle, \tag{12}$$

$$D_{ij} = \langle\psi|n_i n_j|\psi\rangle, \quad \forall i \neq j, \quad D_{ii} = \Pi_{ii} = \rho_i := \langle\psi|n_i|\psi\rangle, \tag{13}$$

define the seniority blocks of the 2-RDM. According to these definitions, it follows that the Π and D matrices are hermitian and fulfill

$$\sum_i \Pi_{ii} = \sum_i D_{ii} = M, \tag{14}$$

$$\sum_j D_{ij} = M\Pi_{ii}, \tag{15}$$

where M is the number of hard-core bosons or particle pairs. The two-positivity conditions in the DOCI space can thus be written in terms of the seniority blocks of the 2-RDM, as previously shown by Weinhold and Wilson[37,38] and others.[23,25,39,41,43] Here, we refer the reader to the Appendix for their complete expressions.

Similarly to the two-positivity conditions, the three-positivity conditions in the seniority-zero subspace can be expressed in terms of the two seniority blocks of the 3-RDM,

$$D_{ijk} = \langle\psi|n_i n_j n_k|\psi\rangle, \quad \forall\ i \neq j \neq k, \tag{16}$$

$$\Pi^i_{jk} = \langle\psi|b^\dagger_j n_i b_k|\psi\rangle = \Pi^i_{kj} = \langle\psi|b^\dagger_k n_i b_j|\psi\rangle, \quad \forall\ i \neq j,k. \tag{17}$$

These blocks may be related to the 2-RDM counterparts as

$$\rho_i = \frac{1}{M-1}\left(\sum_{j<i}\Pi^j_{ii} + \sum_{i>j}\Pi^i_{jj}\right), \quad \forall\ i, \tag{18}$$

$$\Pi_{ij} = \frac{1}{M-1}\sum_{k\neq ij}\Pi^k_{ij}, \quad \forall\ i<j, \tag{19}$$

$$D_{ij} = D_{iij} = \Pi^j_{jj} = \Pi^j_{ii}, \tag{20}$$

$$\Pi^i_{jj} = \frac{1}{M-2}\sum_{k\neq ij} D_{ijk}, \quad \forall\ i<j. \tag{21}$$

The three-positivity conditions were partially formulated in Refs. 37 and 38 and extended further in Refs. 39 and 41. The complete set of three-positivity constraints in the DOCI space, which are also given in the Appendix, has been reported and successfully applied very recently to molecular compounds and pairing Hamiltonians,[26] showing an important improvement upon the results obtained using only two- and partial-three-particle N-representability conditions. However, as we shall show in Sec. III, these conditions may not be sufficient to obtain an accurate description of other strongly correlated models, and therefore, higher order constraints may become necessary. Here, we will derive the complete set of four-positivity conditions in the DOCI space. As in the 2- and 3-RDM cases, the four-positivity conditions in the full Hilbert space [Eqs. (7)] can be drastically simplified if the wave function is restricted to the DOCI space. Within this space, all operators evaluated between two DOCI wave functions need to have seniority-zero and hence cannot change the number of broken particle pairs. This immediately implies that the matrices in Eq. (7) are separated into blocks according to the seniority number of the five different choices of the $B^\dagger$ operators in Eq. (4). The resulting conditions can be written in terms of the three hermitian seniority blocks of the 4-RDM,

$$D_{ijkl} = \langle\psi|n_i n_j n_k n_l|\psi\rangle, \quad \forall i \neq j \neq k \neq l, \tag{22}$$

$$\Pi^{ij}_{kl} = \langle\psi|b^\dagger_k b_l n_i n_j|\psi\rangle, \quad \forall\ i \neq j \neq k \neq l, \tag{23}$$

$$\Pi_{ijkl} = \langle\psi|b^\dagger_i b^\dagger_j b_l b_k|\psi\rangle, \quad \forall\ i \neq j \neq k \neq l, \tag{24}$$

whose elements satisfy the following consistency relations with the 2- and 3-RDMs:

$$\begin{aligned}
&\sum_{j\neq il}\Pi^{ij}_{kl} = (M-2)\Pi^i_{kl},\\
&\sum_{i\neq jkl} D_{ijkl} = (M-3)D_{jkl},\\
&\Pi_{ikkj} = \Pi^k_{ij}, \quad \Pi_{ijij} = D_{ij},\\
&\Pi^{ij}_{kk} = D_{ijk}, \quad D_{ijkk} = D_{ijk}.
\end{aligned} \tag{25}$$

The complete set of constraints in the DOCI space for each representation is presented below. It is important to note that, for the conditions that are split into multiple blocks, we will label the blocks with the indices a, b, c, . . ., and the elements inside each block with indices i, j, k, ...

- The 4-$\mathcal{P}$ condition: from the four-particle representation of the 4-RDM, we obtain

$$D_{ijkl} \geq 0, \quad \forall\ i<j<k<l, \tag{26}$$

$$\Pi^{ab}_{ij} \geq 0, \quad \forall a<b, i, j, \tag{27}$$

$$\Pi_{ijkl} \geq 0 \quad \forall i<j, k<l, \quad \text{with matrix indices } ij \text{ and } kl. \tag{28}$$

This condition possesses $O(L^4)$ blocks of dimension $O(1\times 1)$, $O(L^2)$ blocks of dimension $O(L\times L)$, and $O(1)$ blocks of dimension $O(L^2\times L^2)$, respectively.

- The 4-$\mathcal{Q}$ condition: the four-hole representation of the 4-RDM gives rise to

$$1-\rho_i-\rho_j-\rho_k-\rho_l+D_{ij}+D_{ik}+D_{il}+D_{jk}+D_{jl}+D_{kl}-D_{ijk}-D_{ikl}-D_{ijl}-D_{ijk}+D_{ijkl}\geq 0, \quad \forall\ i<j<k<l, \tag{29}$$

$$\Pi_{ij}-\Pi^a_{ij}-\Pi^b_{ij}+\Pi^{ab}_{ij}+\delta_{ij}(1-\rho_a-\rho_b-2\rho_i+D_{ab}+2D_{ia}+2D_{ib}-2D_{iab})\geq 0, \quad \forall a,b,i\neq a,b,j\neq a,b, \tag{30}$$

$$\begin{aligned}
&\Pi_{ijkl}+\delta_{ik}\left(\Pi_{lj}-2\Pi^i_{lj}\right)+\delta_{jk}\left(\Pi_{li}-2\Pi^j_{li}\right)+\delta_{il}\left(\Pi_{kj}-2\Pi^i_{kj}\right)+\delta_{jl}\left(\Pi_{ki}-2\Pi^j_{ki}\right)+\delta_{ik}\delta_{jl}(1-2\rho_i-2\rho_j+4D_{ij})\geq 0,\\
&\forall i,j,k,l \quad \text{with matrix indices } ij \text{ and } kl.
\end{aligned} \tag{31}$$

This condition also possesses $O(L^4)$ blocks of dimension $O(1 \times 1)$, $O(L^2)$ blocks of dimension $O(L \times L)$, and $O(1)$ blocks of dimension $O(L^2 \times L^2)$, respectively.

- The 4-$\mathcal{E}$ condition: the mixed three-particle-one-hole representation of the 4-RDM yields

$$\begin{pmatrix} D_{abc} - D_{abcd} & \Pi^{bc}_{ad} & \Pi^{ac}_{bd} & \Pi^{ab}_{cd} \\ \Pi^{bc}_{ad} & D_{bcd} - D_{abcd} & \Pi^{cd}_{ab} & \Pi^{bd}_{ac} \\ \Pi^{ac}_{bd} & \Pi^{cd}_{ab} & D_{cda} - D_{abcd} & \Pi^{ad}_{bc} \\ \Pi^{ab}_{cd} & \Pi^{bd}_{ac} & \Pi^{ad}_{bc} & D_{dab} - D_{abcd} \end{pmatrix} \geq 0, \quad \forall\ a < b < c, d \neq abc, \tag{32}$$

$$\begin{pmatrix} D_{ijab} & \Pi^{ia}_{jb} & \Pi^{ib}_{aj} \\ \Pi^{ja}_{ib} & \Pi^{a}_{ij} - \Pi^{ab}_{ij} & \Pi_{iajb} \\ \Pi^{jb}_{ia} & \Pi_{ibja} & \Pi^{b}_{ij} - \Pi^{ab}_{ij} \end{pmatrix} \geq 0, \quad \forall\ ij \neq ab. \tag{33}$$

This condition results in $O(L^4)$ blocks of dimension $O(1 \times 1)$ and $O(L^2)$ blocks of dimension $O(L \times L)$.

- The 4-$\mathcal{F}$ condition: from the mixed three-hole-one-particle representation, we obtain

$$\begin{pmatrix} (a) & \Pi_{ab} - \Pi^{c}_{ab} - \Pi^{d}_{ab} + \Pi^{cd}_{ab} & \Pi_{ac} - \Pi^{b}_{ac} - \Pi^{d}_{ac} + \Pi^{bd}_{ac} & \Pi_{ad} - \Pi^{b}_{ad} - \Pi^{c}_{ad} + \Pi^{bc}_{ad} \\ \cdots & (b) & \Pi_{bc} - \Pi^{a}_{bc} - \Pi^{d}_{bc} + \Pi^{ad}_{bc} & \Pi_{bd} - \Pi^{a}_{bd} - \Pi^{c}_{bd} + \Pi^{ac}_{bd} \\ \cdots & \cdots & (c) & \Pi_{cd} - \Pi^{a}_{cd} - \Pi^{b}_{cd} + \Pi^{ab}_{bd} \\ \cdots & \cdots & \cdots & (d) \end{pmatrix} \geq 0, \tag{34}$$

where the matrix is symmetric and the notation () represents

$$(a) = \rho_a - D_{ab} - D_{ac} - D_{ad} + D_{abc} + D_{abd} + D_{acd} - D_{abcd}, \tag{35}$$

and

$$\begin{pmatrix} D_{ij} - D_{ija} - D_{ijb} + D_{ijab} & \Pi^{i}_{ja} - \Pi^{ib}_{ja} + \delta_{ij}\left(\Pi_{ia} - \Pi^{b}_{ia}\right) & a_1 \\ \Pi^{j}_{ia} - \Pi^{jb}_{ia} + \delta_{ij}\left(\Pi_{ja} - \Pi^{b}_{ja}\right) & \Pi^{a}_{ij} - \Pi^{ab}_{ij} + \delta_{ij}(\rho_a - D_{ab} - 2D_{ia} + 2D_{iab}) & a_2 \\ \Pi^{j}_{ib} - \Pi^{ja}_{ib} + \delta_{ij}\left(\Pi_{jb} - \Pi^{a}_{jb}\right) & \Pi_{aijb} + \delta_{ij}\left(\Pi_{ab} - 2\Pi^{i}_{ab}\right) & a_3 \end{pmatrix} \geq 0, \tag{36}$$

with

$$\begin{aligned} a_1 &= \Pi^{i}_{jb} - \Pi^{ia}_{jb} + \delta_{ij}\left(\Pi_{ib} - \Pi^{a}_{ib}\right), \\ a_2 &= \Pi_{ajib} + \delta_{ij}\left(\Pi_{ab} - 2\Pi^{i}_{ab}\right), \quad \text{and} \\ a_3 &= \Pi^{b}_{ij} - \Pi^{ab}_{ij} + \delta_{ij}(\rho_b - D_{ab} - 2D_{ib} + 2D_{iab}). \end{aligned} \tag{37}$$

This condition also results in $O(L^4)$ blocks of dimension $O(1 \times 1)$ and $O(L^2)$ blocks of dimension $O(L \times L)$.

- The 4-$\mathcal{G}$ condition: the mixed two-particle-two-hole representation yields

$$\begin{pmatrix} (ab) & \Pi^{a}_{bd} - \Pi^{ac}_{bd} & \Pi^{b}_{ad} - \Pi^{bc}_{ad} & \Pi^{a}_{bc} - \Pi^{ad}_{bc} & \Pi^{b}_{ac} - \Pi^{bd}_{ac} & \Pi_{abcd} \\ \Pi^{a}_{bd} - \Pi^{ac}_{bd} & (ad) & \Pi^{d}_{ab} - \Pi^{cd}_{ab} & \Pi^{a}_{cd} - \Pi^{ab}_{cd} & \Pi_{adbc} & \Pi^{d}_{ac} - \Pi^{bd}_{ac} \\ \Pi^{b}_{ad} - \Pi^{bc}_{ad} & \Pi^{d}_{ab} - \Pi^{cd}_{ab} & (bd) & \Pi_{bdac} & \Pi^{b}_{cd} - \Pi^{ab}_{cd} & \Pi^{d}_{bc} - \Pi^{ad}_{bc} \\ \Pi^{a}_{bc} - \Pi^{ad}_{bc} & \Pi^{a}_{cd} - \Pi^{ab}_{cd} & \Pi_{acbd} & (ac) & \Pi^{c}_{ab} - \Pi^{cd}_{ab} & \Pi^{c}_{ad} - \Pi^{bc}_{ad} \\ \Pi^{b}_{ac} - \Pi^{bd}_{ac} & \Pi_{bcad} & \Pi^{b}_{cd} - \Pi^{ab}_{cd} & \Pi^{c}_{ab} - \Pi^{cd}_{ab} & (bc) & \Pi^{c}_{bd} - \Pi^{ac}_{bd} \\ \Pi_{cdab} & \Pi^{d}_{ac} - \Pi^{bd}_{ac} & \Pi^{d}_{bc} - \Pi^{ad}_{bc} & \Pi^{c}_{ad} - \Pi^{bc}_{ad} & \Pi^{c}_{bd} - \Pi^{ac}_{bd} & (cd) \end{pmatrix} \geq 0, \tag{38}$$

with, for example,

$$\begin{aligned} (ab) &= D_{ab} - D_{abc} - D_{abd} + D_{abcd}, \\ (bc) &= D_{bc} - D_{abc} - D_{bcd} + D_{abcd}, \end{aligned} \tag{39}$$

$$\begin{pmatrix} D_{ijb} - D_{ijab} & \Pi^{ij}_{ab} & \Pi^{ib}_{ja} + \delta_{ij}\Pi^{b}_{aj} & \Pi^{i}_{jb} - \Pi^{ia}_{jb} \\ \Pi^{ij}_{ab} & D_{ija} - D_{ijab} & \Pi^{ia}_{jb} + \delta_{ij}\Pi^{a}_{bj} & \Pi^{i}_{ja} - \Pi^{ib}_{ja} \\ \Pi^{jb}_{ia} + \delta_{ij}\Pi^{b}_{aj} & \Pi^{aj}_{ib} + \delta_{ij}\Pi^{a}_{bj} & \Pi^{ab}_{ij} + \delta_{ij}(D_{ab} - 2D_{iab}) & \Pi_{abij} \\ \Pi^{j}_{ib} - \Pi^{ja}_{ib} & \Pi^{j}_{ia} - \Pi^{jb}_{ia} & \Pi_{ijba} & \Pi_{ij} - \Pi^{a}_{ij} - \Pi^{b}_{ij} + \Pi^{ab}_{ij} \end{pmatrix} \geq 0, \tag{40}$$

and

$$\Pi_{ilkj} + \delta_{jl}\left(\Pi_{ik} - 2\Pi^{j}_{ik}\right) \geq 0, \quad \text{with matrix indices } ij \text{ and } kl. \tag{41}$$

This last condition results in $O(L^4)$ blocks of dimension $O(1 \times 1)$, $O(L^2)$ blocks of dimension $O(L \times L)$, and $O(1)$ blocks of dimension $O(L^2 \times L^2)$.

In Sec. III, we will discuss the implementation of the variational methodology under these p-positivity conditions and its application to the Heisenberg XXZ spin model.

III. APPLICATION TO HEISENBERG XXZ SPIN MODEL

The Heisenberg Hamiltonian is a fundamental model for quantum magnetism in one dimension.[44] For spin 1/2, the XXZ version of the model is exactly solvable by means of the Bethe ansatz.[45] The Hamiltonian for a chain of L spins reads

$$H = \sum_i \left[\frac{1}{2}(S^+_i S^-_{i+1} + S^-_i S^+_{i+1}) + \Delta S^z_i S^z_{i+1}\right], \tag{42}$$

where $S^{\pm}_i$ and S^z_i represent the fermionic spin-ladder and spin projection operators acting at the site i. The parameter Δ fixes the anisotropy of the model. As a function of Δ, the model has a rich phase diagram. For $-1 < \Delta < 1$, the system is a critical antiferromagnet with gapless excitations. For $|\Delta| > 1$, the system is gapped; however, it is ferromagnetic for $\Delta < -1$ and antiferromagnetic for $\Delta > 1$. In a standard hard-core boson representation, the spin operators can be written as

$$S^+_i = b^\dagger_i = (S^-_i)^\dagger, \quad S^z_i = b^\dagger_i b_i - \frac{1}{2} = n_i - \frac{1}{2}, \tag{43}$$

and the total number of hard-core bosons is related to the z projection of the spin as $\sum_i n_i = M = S^z_{tot} + L/2$, meaning that half-filling ($M/L = 1/2$) corresponds to $S^z_{tot} = 0$. In terms of these hard-core boson operators, the Hamiltonian reads

$$H = \Delta\left(\frac{L}{4} - M\right) + \sum_i \left[\frac{1}{2}(b^\dagger_i b_{i+1} + b^\dagger_{i+1} b_i) + \Delta n_i n_{i+1}\right], \tag{44}$$

yielding the energy functional of the Π and D seniority blocks of the 2-RDM,

$$E = \Delta\left(\frac{L}{4} - M\right) + \sum_i [\Pi_{ii+1} + \Delta D_{ii+1}]. \tag{45}$$

The Hamiltonian (44) has the same form as Eq. (8) with constant pairing and first-neighbor monopole interaction Δ, namely, $\varepsilon_i = \Delta(1/4 - M/L)$, $w_{ij} = \delta_{ji+1}\Delta$, and $v_{ij} = \frac{1}{2}(\delta_{ji+1} + \delta_{ij+1})$. Since the Hamiltonian is particle-hole symmetric under the transformation $h_i = b^\dagger_i$, $h^\dagger_i = b_i$, the off-diagonal elements of the Π block of the 2-RDM for systems with M and $L - M$ hard-core bosons are equal. Only the diagonal elements change, and they satisfy the relation $\rho^{(M)}_i = 1 - \rho^{(L-M)}_i$. Furthermore, the particle-hole symmetry also implies the relation $D^{(L-M)}_{ij} - \rho^{(L-M)}_i = D^{(M)}_{ij} - \rho^{(M)}_j$ for the D block of the 2-RDM so that the properties of a system with M hard-core bosons are mapped to those with $L - M$ hard-core bosons.

For vanishing Δ, the system can also be mapped to a set of non-interacting fermions through the Jordan-Wigner transformation[46] and thus, the two-positivity conditions on those fermions must be sufficient N-representability conditions; however, it must be emphasized that the two-positivity conditions of the hard-core bosons are not sufficient. On the other hand, for $\Delta = -1$, the exact ground state of the XXZ model is an antisymmetrized geminal power (AGP) state

$$|\Psi\rangle_{\Delta=-1} = \left[\sum_i (-1)^i b^\dagger_i\right]^M |0\rangle, \tag{46}$$

with energy $E = -L/4$. As is well known,[1,47] the energy of an AGP ground state can exactly be calculated within the two-positivity conditions in the v2RDM-DOCI treatments since the 2-$\mathcal{G}$ condition included in that constraint set guarantees the exactness of the energy variationally calculated for this type of Hamiltonians. However, it does not imply that the calculated 2-RDM is exact since compensation of errors in the energy can occur.

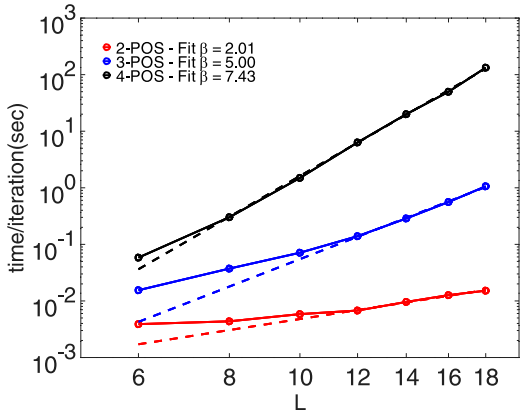

FIG. 1. Scaling of the v2RDM-DOCI computing time under 2-, 3-, and 4-POS conditions as a function of the chain length L for systems at half-filling on a log-log plot. Each computation requires between 20 and 40 iterations to reach convergence in the SDP program. Linear fitting (dashed lines) of the form $\beta x + \alpha$ is included. Simulations were run single-threaded on an Intel Xeon E5-2650v2.

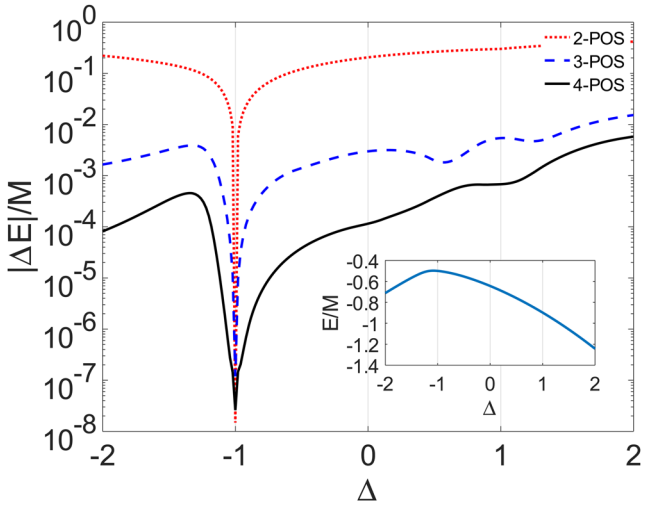

FIG. 2. Energy error per particle pair $\Delta E/M = (E_{\text{exact}} - E_{\text{v2RDM-DOCI}})/M$ (in logarithmic scale) for a chain of $L = 12$ sites at half filling as function of the anisotropy Δ. The 2-, 3-, and 4-POS results are depicted in dotted, dashed, and solid lines, respectively. The inset shows the exact energy as function of Δ.

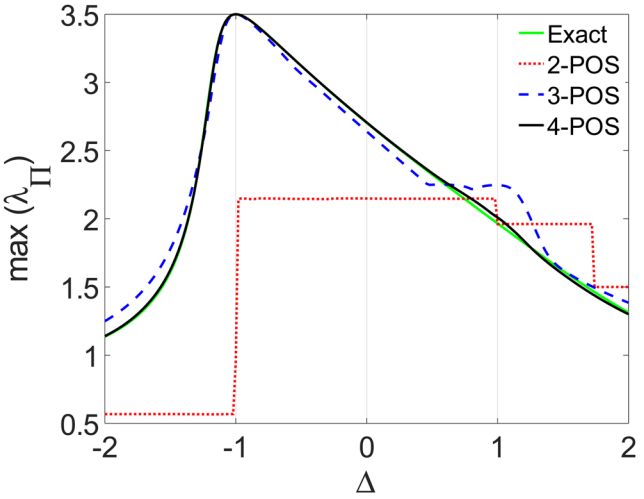

FIG. 4. Largest eigenvalue of the Π block of the 2-RDM as a function of Δ for a chain of $L = 12$ sites at half filling.

The variational optimization of the 2-RDM for the ground state of the Heisenberg XXZ model was performed for three sets of N-representability conditions: the two-positivity conditions (2-POS), the three-positivity conditions (3-POS), and the four-positivity conditions (4-POS). These sets of N-representability conditions are supplemented with their hermiticity and normalization relations, together with the contractions and consistency relations corresponding to each set of conditions. These optimizations have been formulated as a semidefinite problem (SDP) in which the energy, being a linear function of the 2-RDM, is minimized over the intersection of a linear affine space and the convex cone of block-diagonal positive semidefinite matrices.[48–51] We have developed codes that allow us to efficiently formulate and solve the SDP exploiting the sparse structure of the matrices from the three sets of p-positivity conditions induced by the structure of the seniority-zero wave functions. Thus, the SDP in the seniority-zero subspace computationally scales with the number L of single-particle basis elements as $O(L^3)$, $O(L^4)$, and $O(L^6)$ for the 2-, 3-, and 4-POS conditions, respectively. This scaling is due to the sparse structure of the four-particle metric matrices within the DOCI framework, as explained in the discussion of Eqs. (26)–(41). This will allow us to treat with minimal computational effort systems of medium size. In Fig. 1, we show the computing time for the v2RDM-DOCI treatment under the 2-, 3-, and 4-POS conditions as a function of L, both in logarithmic scale. We perform a linear fit to find the power of the leading term in the scaling ($\propto L^{\beta}$). This fit has been done using only the last four points of the calculated data sets, trying to avoid the low-scaling operations that dominate the computing time for small systems. As can be seen, this fit provides numerical scalings that deviate from the theoretical ones due to the implementation of the SDPA algorithm. On the other hand, as the DOCI energy is not invariant to single-particle basis rotations, in cases where optimal basis are required, the optimization step might scale as $O(L^5)$. We programmed our variational reduced density matrix method as a dual problem in the semidefinite programming algorithm (SDPA) code,[28,29] which solves semidefinite problems at several precision levels by means of the Mehrotra-type predictor-corrector primal-dual interior-point method, providing

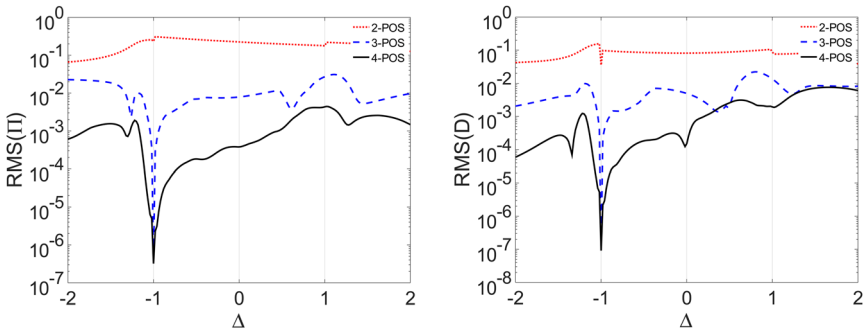

FIG. 3. RMS of the Π (left panel) and D (right panel) blocks of the 2-RDM as a function of Δ for a chain of $L = 12$ sites at half filling.

ground-state energies and the corresponding 2-RDMS. As this code does not allow for equality constraints as those arising from the normalization and consistency relations, they have been included by relaxing them into inequality constraints with a sufficiently small summation error.[8] In our calculations, we have set $\delta = 10^{-7}$, which effectively fixes the precision of the ground-state energies. The v2RDM-DOCI results will be compared with exact calculations performed by exact diagonalization of the Hamiltonian (44).

We first analyze the accuracy of the 4-POS conditions in a chain of $L = 12$ sites at half filling ($M = L/2$) as compared to 2-POS and 3-POS conditions. In Fig. 2, we present results for the energy error $\Delta E = E_{\text{exact}} - E_{\text{v2RDM-DOCI}}$ as functions of the anisotropy parameter Δ. For $\Delta = -1$, we confirm that already the 2-POS conditions yield numerically exact energies as expected for the AGP state [Eq. (46)]. On the other hand, for arbitrary Δ, the accuracy of the v2RDM-DOCI with the 4-POS conditions is about an order of magnitude higher than the 3-POS results. The variationally calculated 2-RDMs at the 2-POS condition level are expected to be inaccurate as we have numerically verified. Consequently, similar trends can be observed in the root-mean-square (RMS) errors of the Π and D blocks of the 2-RDM. For a given approximated matrix A,

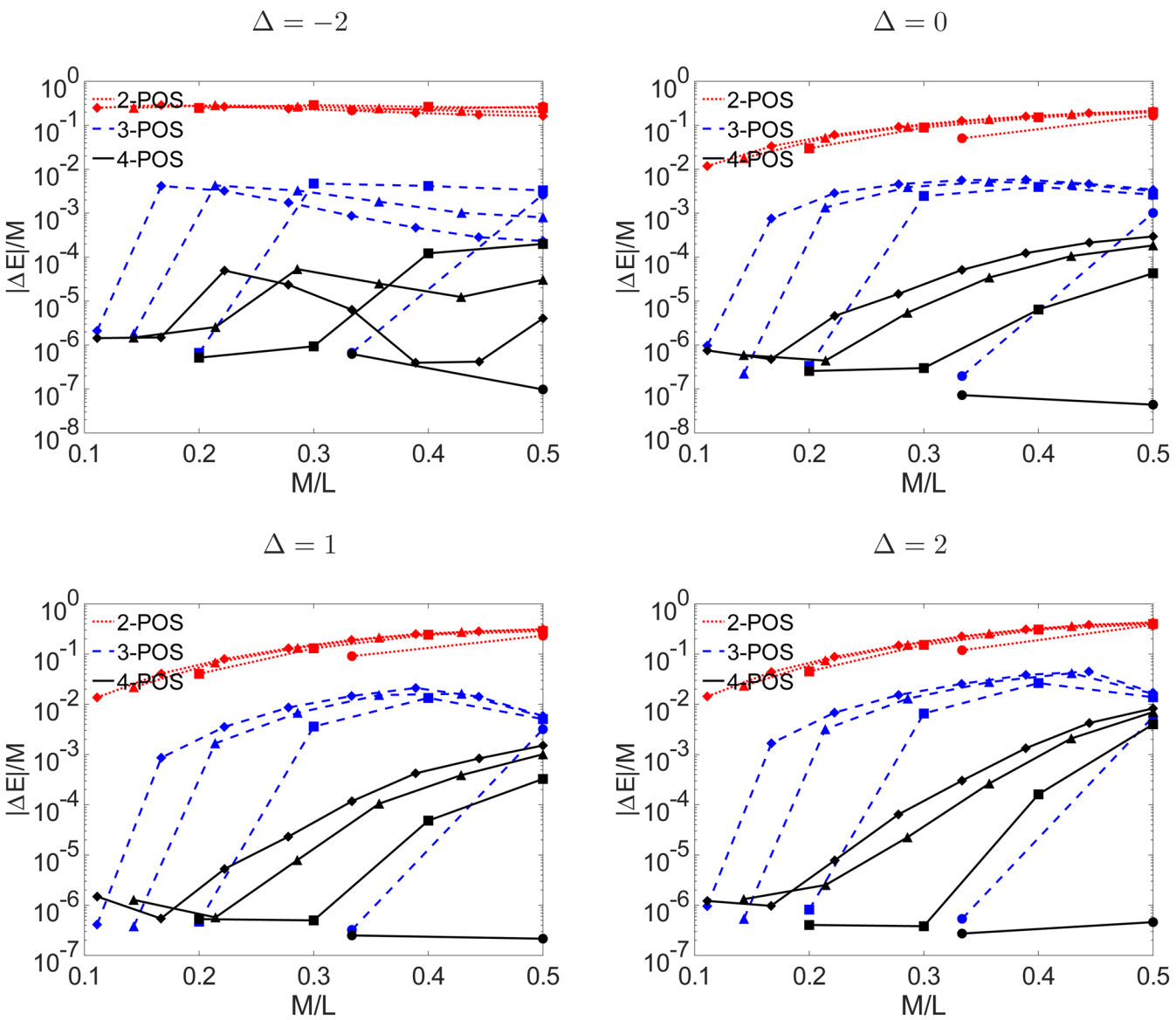

FIG. 5. Energy error per particle pair $\Delta E/M = (E_{\text{exact}} - E_{\text{v2RDM-DOCI}})/M$ (in logarithmic scale) for chains of $L = 6$ (circles), 10 (squares), 14 (triangles), and 18 (diamonds) sites as functions of the filling M/L for $\Delta = -2$ (top left panel), 0 (top right panel), 1 (bottom left panel), and 2 (bottom right panel).

these errors are defined as $\mathrm{RMS}(A) = \sqrt{\sum_{ij}(A_{ij} - A_{ij}^{\mathrm{exact}})^2}/L$. In Fig. 3, we show the RMS for the $L = 12$ chain at half filling. As it can be seen, the 2-POS condition furnishes an accuracy of about 10^{-1} in the range $\Delta \in [-2, 2]$. However, at $\Delta = -1$, the errors of the Π and D seniority blocks of the 2-RDM cancel each other in Eq. (45), yielding the exact energy. On the other hand, the 3-POS and 4-POS provide an upper bound to the accuracy of approximately one order of magnitude each set of conditions, namely, 10^{-2} and 10^{-3}, respectively. These results at half filling are consistent with previous observations in the literature.[40,52,53]

The improvement in the energy and in the RMS of the seniority blocks of the 2-RDMs offered by the 4-POS with respect to the 3-POS conditions may seem modest for some values of Δ; however, the ground state of the XXZ Hamiltonian changes qualitatively from a ferromagnetic phase for $\Delta \leq -1$ to an antiferromagnetic phase for $\Delta \geq 1$ and the 4-POS conditions particularly improve the energy in the antiferromagnetic phase. The importance of the 4-POS can be better elucidated in the calculation of the largest eigenvalue of the Π block of the 2-RDM, λ_Π, which measures the presence of off-diagonal long-range order (ODLRO) in the system. The results obtained within the 2-, 3-, and 4-POS conditions are compared with those from exact calculation in Fig. 4. As can be seen, the 2-POS conditions fail dramatically, leading to an incorrect (unphysical) structure of the 2-RDM, mainly at one of the phase transition points ($\Delta = -1$). On the other hand, around $\Delta = 1$, the accuracy of the 3-POS conditions is unable to provide a correct description of the ODLRO, while 4-POS barely deviates from the exact calculation. Therefore, one expects that the 4-POS condition could improve the description of such types of transitions.

We have also examined the accuracy of the 2-, 3-, and 4-POS representability conditions for varying fillings M/L and chain lengths L from $L = 6$ to 18. Due to the particle-hole symmetry, we have only calculated results for M particle pairs ranging from 2 to $L/2$. The results for the energy errors are summarized in Fig. 5 for the values of $\Delta = -2, 0, 1$, and 2. It must be noted that the p-positivity conditions become sufficient to guarantee the N-representability of the 2-RDM in the variational calculations for systems with $M = p/2$ particle pairs. In these cases, the numerical errors stem from the imposed precision, δ, on the SPDA calculations. On the other hand, the results at moderate fillings show a maximum error reduction of about an order of magnitude, with the absolute error per hard-core boson $|\Delta E|/M$ reaching about 2×10^{-5} in the ferromagnetic phase and about 3×10^{-3} in the antiferromagnetic one, both for the largest chain considered $L = 18$. At lower filling, the errors are slightly reduced for $\Delta > 0$. Moreover, it follows that in general, for a given L, the energy errors per particle pairs increase with M, suggesting that additional N-representability conditions may be required to obtain the desired accuracy. Finally, we found that for a given filling, the variational errors generally increase with system size, reaching a constant limit. This is consistent with previous observations in the literature[25,41] that no size-extensivity issues are found in this variational approach.

IV. SUMMARY AND CONCLUSIONS

We have implemented a treatment for the variational determination of the two-particle reduced density matrix arising from doubly occupied-configuration-interaction N-electron wave functions, using up to four-particle N-representability conditions. These variational constraints are necessary conditions which must be satisfied so that the resulting two-particle reduced density matrix can be regarded as N-representable. The formalism has been presented in terms of hard-core bosons and tested with the spin 1/2 XXZ model as a representative model of a strongly correlated system within the class of seniority-zero Hamiltonians. It can also be directly applied to the description of N-electron atomic and molecular systems within the DOCI framework, provided that the corresponding optimal single-particle basis is constructed. We describe variationally computed ground-state energies, two-particle reduced density matrix elements, and correlation functions across a full range of Hamiltonian parameters. The results obtained with the four-particle N-representability conditions show a significant improvement over the previously reported results using two- and three-particle N-representability conditions, despite that this improvement entails an additional increase in the computational cost. The quality of these results indicates that the four-particle variational constraint conditions could improve significantly the quality of the results at an affordable computational cost within the field of application of the doubly occupied-configuration-interaction framework.

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APPENDIX: POSITIVE SEMIDEFINITENESS CONDITIONS FOR N-REPRESENTABILITY OF THE 2- AND 3-RDM IN THE DOCI SPACE

As mentioned in Sec. II, restricting the operator $B^\dagger$ in Eq. (4) to the two-particle space leads to the 2-$\mathcal{P}$, 2-$\mathcal{Q}$ and 2-$\mathcal{G}$ N-representability conditions. In the seniority-zero subspace, the 2-RDM becomes block diagonal in the seniority number and these conditions can be reformulated in terms of their seniority blocks Π and D. Thus, it follows that:[23,25,37–39,41,43]

- the 2-$\mathcal{P}$ condition:

$$\Pi_{ij} \geq 0, \tag{A1}$$

$$D_{ij} \geq 0, \quad \forall i, j, \tag{A2}$$

- the 2-$\mathcal{Q}$ condition:

$$\Pi_{ij} + \delta_{ij}(1 - 2\rho_i) \geq 0, \tag{A3}$$

$$D_{ij} + 1 - \rho_i - \rho_j \geq 0, \quad \forall i < j, \tag{A4}$$

- the 2-$\mathcal{G}$ condition:

$$\begin{pmatrix} \rho_a - D_{ab} & -\Pi_{ab} \\ -\Pi_{ba} & \rho_b - D_{ab} \end{pmatrix} \geq 0, \quad \forall a < b, \tag{A5}$$

$$D_{ij} \geq 0. \tag{A6}$$

Similarly, in the seniority-zero subspace, the three-positivity conditions 3-$\mathcal{P}$, 3-$\mathcal{Q}$, 3-$\mathcal{E}$, and 3-$\mathcal{F}$ can be expressed in terms of the two seniority blocks of the 3-RDM [Eqs. (16) and (17)] as follows:

- the 3-$\mathcal{P}$ condition:

$$D_{ijk} \geq 0, \quad \forall\, i < j < k, \tag{A7}$$

$$\Pi^a_{ij} \geq 0, \quad \forall a, \tag{A8}$$

- the 3-$\mathcal{Q}$ condition:

$$1 - \rho_i - \rho_j - \rho_k + D_{ij} + D_{jk} + D_{ki} - D_{ijk} \geq 0, \quad \forall\, i < j < k, \tag{A9}$$

$$-\Pi^a_{ij} + \Pi_{ji} + \delta_{ij}(1 - 2\rho_i - \rho_a + 2D_{ia}) \geq 0, \quad \forall\, ij \neq a, \tag{A10}$$

- the 3-$\mathcal{E}$ condition:

$$\begin{pmatrix} D_{ab} - D_{abc} & \Pi^a_{bc} & \Pi^b_{ac} \\ \Pi^a_{bc} & D_{ac} - D_{abc} & \Pi^c_{ab} \\ \Pi^b_{ac} & \Pi^c_{ab} & D_{bc} - D_{abc} \end{pmatrix} \geq 0, \quad \forall\, a < b < c, \tag{A11}$$

$$\begin{pmatrix} D_{aij} + \delta_{ij} D_{ai} & \Pi^i_{aj} & D_{ia} \\ \Pi^j_{ai} & \Pi_{ij} - \Pi^a_{ij} & \Pi_{ia} \\ D_{ai} & \Pi_{ai} & \rho_a \end{pmatrix} \geq 0, \quad \forall\, a, ij \neq a, \tag{A12}$$

- the 3-$\mathcal{F}$ condition:

$$\begin{pmatrix} \rho_a - D_{ab} - D_{ac} + D_{abc} & \Pi_{ac} - \Pi^b_{ac} & \Pi_{ab} - \Pi^c_{ab} \\ \Pi_{ac} - \Pi^b_{ac} & \rho_c - D_{bc} - D_{ac} + D_{abc} & \Pi_{bc} - \Pi^a_{bc} \\ \Pi_{ab} - \Pi^c_{ab} & \Pi_{bc} - \Pi^a_{bc} & \rho_b - D_{ab} - D_{bc} + D_{abc} \end{pmatrix} \geq 0, \quad \forall\, a < b < c, \tag{A13}$$

$$\begin{pmatrix} -D_{aij} + \delta_{ij}(\rho_i - D_{ai}) + D_{ij} & -\Pi^i_{aj} - \delta_{ij}\Pi_{ia} & \rho_i - D_{ia} \\ -\Pi^i_{aj} - \delta_{ij}\Pi_{ia} & \Pi^a_{ij} + \delta_{ij}(\rho_a - 2D_{ia}) & -\Pi_{ia} \\ \rho_i - D_{ai} & -\Pi_{ai} & 1 - \rho_a \end{pmatrix} \geq 0, \quad \forall\, a, ij \neq a. \tag{A14}$$

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