JCTC Journal of Chemical Theory and Computation

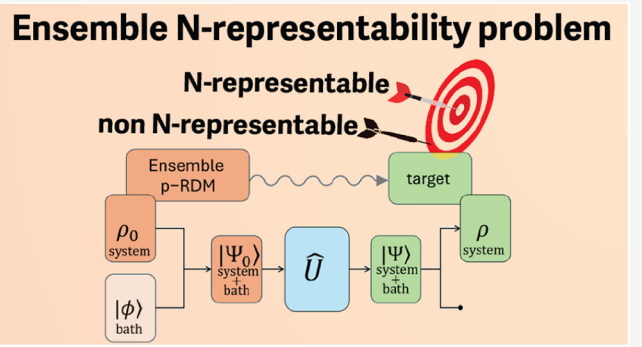
pubs.acs.org/JCTC Article

Determining the Ensemble *N*-Representability of Reduced Density Matrices

Ofelia B. Oña, Gustavo E. Massaccesi, Pablo Capuzzi, Luis Lain, Alicia Torre, Juan E. Peralta,* Diego R. Alcoba,* and Gustavo E. Scuseria*

Cite This: *J. Chem. Theory Comput.* 2026, 22, 399−406 Read Online

ABSTRACT: The *N*-representability problem for reduced density matrices remains a fundamental challenge in electronic structure theory. Following our previous work that employs a unitary-evolution algorithm based on an adaptive derivative-assembled pseudo-Trotter variational quantum algorithm to probe *pure-state* *N*-representability of reduced density matrices [J. Chem. Theory Comput. 2024, 20, 9968], in this work we propose a practical framework for determining the *ensemble* *N*-representability of a *p*-body matrix. This is accomplished using a purification strategy that embeds an ensemble state into a pure state defined on an extended Hilbert space, such that the reduced density matrices of the purified state reproduce those of the original ensemble. By iteratively applying variational unitaries to an initial purified state, the proposed algorithm minimizes the Hilbert-Schmidt distance between its *p*-body reduced density matrix and a specified target *p*-body matrix, which serves as a measure of the *N*-representability of the target. This methodology facilitates both error correction of defective ensemble reduced density matrices and quantum-state reconstruction on a quantum computer, offering a route for density-matrix refinement. We validate the algorithm with numerical simulations on systems of two, three, and four electrons in both simple models as well as molecular systems at finite temperature, demonstrating its robustness.



INTRODUCTION

The significance of the *N*-representability problem in electronic structure theory is both foundational and far-reaching.[1] At the heart of this challenge lies the quest to determine the necessary and sufficient conditions that a *p*-body reduced density matrix (*p*-RDM) must satisfy to be derivable from a *N*-electron wave function or mixed (ensemble) state.[2−9] The special case of the 2-RDM is essential for the development of quantum chemistry computational methods.[2,3,10] Equally important, though often less emphasized, is the role of the 1-RDM in practical applications, such as in Hartree−Fock and density (matrix) functional theory, where the 1-RDM serves as a cornerstone for calculating observable properties.[11−13] Despite its theoretical interest, the *N*-representability problem presents formidable computational challenges. It belongs to the quantum Merlin-Arthur-complete class of problems: a quantum analog of the well-known nondeterministic polynomial-time complete class in classical complexity theory.[14] This classification implies that, in general, verifying whether a given *p*-RDM corresponds to a physical *N*-electron state is computationally intractable, especially as system size increases. Recent developments have led to sets of approximate *N*-representability conditions that, while not exhaustive, are sufficiently robust to enable meaningful calculations for strongly correlated electron systems, particularly in small to medium-sized molecules.[10,15−20] Moreover, Coleman[4] and Klyachko[21,22] derived the necessary and sufficient *N*-representability conditions that must be fulfilled by the 1-RDM to be derivable from an ensemble or pure *N*-Fermion quantum state, respectively. These conditions, which constrain the eigenvalues of the 1-RDM, offer a mathematically rigorous framework for identifying physically valid Fermionic occupation numbers.[2,22−31]

In recent work, we introduced an algorithm[32] designed to numerically determine whether a given *p*-body reduced density matrix (*p*-RDM) is pure *N*-representable, or in other words, whether it can be obtained by tracing out (*N*−*p*) degrees of freedom from a pure *N*-body quantum state (i.e., a single wave function or pure-state density matrix). The proposed algorithm operates by guiding the unitary evolution of an ansatz wave function through its corresponding *p*-RDM toward a target

Received: October 24, 2025
Revised: December 9, 2025
Accepted: December 12, 2025
Published: December 26, 2025

https://doi.org/10.1021/acs.jctc.5c01788
J. Chem. Theory Comput. 2026, 22, 399−406

matrix (alleged p-RDM), with the goal of minimizing their Hilbert-Schmidt distance (a measure of how close two matrices are in Hilbert space). The evolution (driven by stochastic sampling in that work) is inspired by the adaptive derivative-assembled pseudo-Trotter (ADAPT) framework, originally developed for the variational quantum eigensolver (VQE) problem,[33] and other approaches related to it, including the contracted quantum eigensolver.[34−41] As such, the algorithm is suited for implementation on quantum devices.[33,42,43] We refer to this approach as pure ADAPT-VQA (Variational Quantum Algorithm), and its utility extends beyond mere classification. Not only can it determine whether a given matrix is a valid pure p-RDM, but it can also correct matrices that fail to meet the N-representability criteria. This dual capability makes the pure ADAPT-VQA a powerful tool for quantum simulations, offering a pathway to enforce physical constraints in quantum algorithms and potentially improve the accuracy of quantum chemical calculations.

In this work, we address a critical extension of the N-representability problem, namely, its formulation for ensemble p-RDMs.[2,3] While part of the existing literature focuses on pure-state representability,[2,22−30,44] ensemble states are equally important, especially in contexts involving thermal mixtures, open quantum systems, and statistical ensembles.[2,3] To address this challenge, we employ a purification-based method in which the ensemble state is represented as a pure state within an expanded Hilbert space,[45,46] which has been recently applied to finite temperature electronic systems through the thermofield theory.[47−49] This method ensures that the reduced density matrices of both the ensemble and its purified counterpart are identical, allowing us to leverage techniques developed for pure states. Specifically, we apply the pure ADAPT-VQA algorithm introduced in our previous work,[32] which enables the unitary evolution of the purified state to minimize the Hilbert-Schmidt distance between its p-RDM and a given target matrix. Building on this foundation, we introduce a new algorithm, the ensemble ADAPT-VQA, which extends the capabilities of its pure-state predecessor. This hybrid framework allows us not only to determine whether a p-body matrix is N-representable, but also to discern the nature of its origin: whether it arises from a pure quantum state or from an ensemble mixture of pure states. Such a distinction is crucial for interpreting quantum simulations and for enforcing physical constraints in variational algorithms. To validate the performance and versatility of ensemble ADAPT-VQA, we conduct numerical experiments on both model and molecular systems. Specifically, we test the algorithm on the 1-RDM and 2-RDM of four-electron systems at zero temperature, as well as on the H_2 and H_3 molecules at finite temperature. These examples demonstrate the ability of the algorithm to handle pure and thermal-state scenarios, highlighting its potential for broader applications in quantum chemistry and quantum information.

THEORETICAL CONSIDERATIONS

Let us consider a quantum mixed (ensemble) state, ρ, defined on a finite-dimensional Hilbert space $\mathcal{H}_s$, which can be expressed as

$$\rho = \sum_i p_i |\phi_i\rangle\langle\phi_i| \tag{1}$$

where $|\phi_i\rangle \in \mathcal{H}_s$ are pure-state wave functions, and p_i probabilities satisfying $p_i \geq 0$ with $\sum_i p_i = 1$. According to the Schrödinger-Hughston-Jozsa-Wootters theorem,[50] any such mixed state ρ admits a purification: there exists an auxiliary finite-dimensional Hilbert space $\mathcal{H}_b$ and a pure-state wave function $|\Psi_{sb}\rangle \in \mathcal{H}_{sb}$ (with $\mathcal{H}_{sb} = \mathcal{H}_s \otimes \mathcal{H}_b$ an extended Hilbert space), referred to as a purification of ρ, such that[45]

$$\rho = \mathrm{Tr}_b(|\Psi_{sb}\rangle\langle\Psi_{sb}|) \tag{2}$$

where Tr_b implies the complete trace over the degrees of freedom on the auxiliary Hilbert space $\mathcal{H}_b$. Moreover, every purification of ρ can be written in the form

$$|\Psi_{sb}\rangle = \sum_i \sqrt{p_i}|\phi_i\rangle \otimes |b_i\rangle \tag{3}$$

where $\{|b_i\rangle\}_i$ is an orthonormal basis of $\mathcal{H}_b$. Thus, one can use this strategy to embed an ensemble state into a pure state defined in an extended Hilbert space, such that the p-RDMs of the purified ensemble are reproduced by those of the pure state.

Equation 3 provides a practical approach to numerically determine the ensemble N-representability of a p-RDM by unitarily evolving a pure state. This can be accomplished using an algorithm that has been recently introduced by us to deal with the pure N-representability problem.[32] Here we summarize the newly proposed algorithm employed for the ensemble case. The underlying idea is to find a sequence of unitary transformations that evolve an initial $2N$-particle wave function $|\Psi_0\rangle$ built according to eq 3, e.g.,

$$|\Psi_0\rangle = |\phi_0\rangle \otimes |\phi_0\rangle \tag{4}$$

with $|\phi_0\rangle$ holding N particles. The evolution is such that the Hilbert-Schmidt distance $\mathcal{D}$ between the p-RDM corresponding to the evolved state $|\Psi_k\rangle$,

$${}^p\rho_k = p!\binom{N}{p}\mathrm{Tr}_{N-p}(\mathrm{Tr}_b(|\Psi_k\rangle\langle\Psi_k|)) \tag{5}$$

and a given (possibly) ensemble N-representable target p-RDM, ${}^p\rho_{\mathrm{target}}$, is minimized. The (squared) distance is calculated according to the Hilbert−Schmidt norm,

$$\mathcal{D}_k = \|{}^p\rho_k - {}^p\rho_{\mathrm{target}}\|_2^2 \tag{6}$$

At convergence, the ADAPT-VQA yields a minimum feasible distance for the problem at hand, $\mathcal{D}_{\mathrm{min}}$, and the state $|\Psi_{\mathrm{min}}\rangle$. Thus, if the algorithm evolves the distance $\mathcal{D}_k$ to numerical zero, then ${}^p\rho_{\mathrm{target}}$ is ensemble N-representable. In general, $\mathcal{D}_{\mathrm{min}}$ can be considered as a measure of the degree of ensemble N-representability of ${}^p\rho_{\mathrm{target}}$, and the evolved ${}^p\rho$ is an ensemble N-representable (physical) reduced state that is closest to ${}^p\rho_{\mathrm{target}}$. Hence, the algorithm allows to correct the possible error associated with the lack of ensemble N-representability of ${}^p\rho_{\mathrm{target}}$.

The minimization algorithm employed in this work is schematized in Algorithm 1. The procedure follows the schemes previously introduced by us to determine the N-representability of pure RDMs and transition RDMs.[32,51] In the present work, we adopt the same gradient-based strategy utilized for transition RDMs, in combination with an antihermitian excitation-deexcitation operator pool $\{\hat{O}\}$ suitable for Fermions,[52−55]

https://doi.org/10.1021/acs.jctc.5c01788
J. Chem. Theory Comput. 2026, 22, 399−406

Algorithm 1 Distance ($\mathscr{D}$) minimization algorithm

Input: Target ${}^{p}\rho_{\text{target}}$ and initial state $|\Psi_0\rangle$ defined over an extended Hilbert space $\mathscr{H}_{sb}$.
Output: $\mathscr{D}_{\min}$, $|\Psi_{\min}\rangle$.

```
Prepare operator pool {Ô} corresponding to 𝓗_sb.
procedure
  while k < k_max and |𝒟_k − 𝒟_{k−1}| > δ do
    for Ô ∈ {Ô} do
      Minimize distance to the target ᵖρ_target for |Ψ⟩ = e^{θÔ}|Ψ_{k−1}⟩ with respect to θ.
    end for
    Keep Ô_min and the corresponding θ_min that give the minimum distance 𝒟.
    The new state is |Ψ_k⟩ = e^{θ_min Ô_min}|Ψ_{k−1}⟩.
    𝒟_k ← 𝒟_min , |Ψ_k⟩ ← |Ψ_min⟩.
    k ← k + 1.
  end while
end procedure
```

$$\hat{O}_{ik} = \hat{a}_i^{\dagger}\hat{a}_k - \hat{a}_k^{\dagger}\hat{a}_i \tag{7}$$

and

$$\hat{O}_{ijkl} = \hat{a}_i^{\dagger}\hat{a}_j^{\dagger}\hat{a}_k\hat{a}_l - \hat{a}_k^{\dagger}\hat{a}_l^{\dagger}\hat{a}_i\hat{a}_j \tag{8}$$

for one- and two-particle excitations, respectively. In eqs 7 and 8, $\hat{a}^{\dagger}$ and $\hat{a}$ are the usual Fermionic creation and annihilation operators acting on an orthonormal finite single-particle basis associated with the extended Hilbert space $\mathscr{H}_{sb}$. Furthermore, since we opt to work on a canonical ensemble framework, the operator pool is restricted in such a way that no electronic transitions changing the number of particles in the system of interest nor in the auxiliary system are allowed. In practice, the operators in eqs 7 and 8 are represented as a combination of Pauli operators via the Jordan-Wigner transformation,[56] ensuring that the proposed algorithm is suitable for simulations on quantum computers.[57]

COMPUTATIONAL DETAILS

The implementation of the algorithm described in the previous section utilizes an in-house code written in Python that uses OpenFermion[58] for the Jordan-Wigner mapping and the OpenFermion module of PySCF[59,60] for integral computation and manipulation. Computations reported in this work are carried out on a simulated noiseless quantum device. The original ensemble N-electron problem is embedded into a extended pure $2N$-electron problem (eq 3). The former uses K spatial orbitals as single-particle basis, while the latter uses $2K$ orbitals. For the 4-electron model systems at zero temperature, we use $K = 3$ and $K = 4$ single-particle spatial orbitals, referred to as $(4e, 3o)$ and $(4e, 4o)$ hereafter, while for the H_2 and H_3 molecular systems at finite temperature we use STO-3G basis set ($K = 2$ and $K = 3$, respectively). This choice allows us to deal with 1- and 2-RDMs, which are commonly the most relevant for electronic structure problems, while keeping the computations tractable. This leads to a pool of 378 and 1196 operators for the $(4e, 3o)$, $(4e, 4o)$, respectively, while for the H_2 and H_3 molecular cases the number of operators in the pool is 72, and 378, respectively. The convergence threshold, δ, in the iterative process (Algorithm 1) is varied within the range $[5 \times 10^{-9}, 3 \times 10^{-5}]$. A smaller δ is used for stricter convergence requirements, such as for N-representable one-body targets, while δ is increased for two-body targets and in cases of a stronger N-representability violation. Details of the number of iterations to reach convergence are available in the (Supporting Information SI).

RESULTS AND DISCUSSION

Model Systems at Zero Temperature. Given a p-RDM, one can determine if it is pure N-representable utilizing the previously proposed pure ADAPT-VQA. If the p-RDM results non pure N-representable, one can utilize the ensemble ADAPT-VQA proposed in this work to determine its ensemble N-representability. Thus, the two algorithms serve to classify a p-RDM as pure or ensemble N-representable. We first test this idea to numerically determine if the 1- and 2-RDMs of two analytical model systems are pure or ensemble N-representable. To assess the validity of our numerical results, we make use of Klyachko's N-representability inequalities (also known as generalized Pauli conditions), which provide a set of necessary and sufficient analytical constraints that pure 1-RDMs must satisfy.[21,22] For the $(4e, 3o)$ and $(4e, 4o)$ model systems, we construct target p-RDMs as

$${}^{p}\rho_{\text{target}} = p!\binom{N}{p}\text{Tr}_{N-p}(\rho) \tag{9}$$

where the state ρ is a convex linear combination of two pure states, ρ_1 and ρ_2 (shown in Table 1),

$$\rho = w\rho_1 + (1-w)\rho_2 \quad 0 \le w \le 1 \tag{10}$$

Table 1. States Used to Construct the Target RDMs for the $(4e, 3o)$ and $(4e, 4o)$ Model Systems in eq 2

	State	
Model system	ρ_1	ρ_2
$(4e, 3o)$	$\|1^{\alpha}\ 1^{\beta}\ 2^{\alpha}\ 2^{\beta}\rangle$	$\|1^{\alpha}\ 1^{\beta}\ 3^{\alpha}\ 3^{\beta}\rangle$
$(4e, 4o)$	$\|1^{\alpha}\ 1^{\beta}\ 2^{\alpha}\ 2^{\beta}\rangle$	$\|1^{\alpha}\ 1^{\beta}\ 3^{\alpha}\ 2^{\beta}\rangle$

The parameter w in eq 10 is set to a value of 0.0 or 0.5 for ρ representing either a pure, or mixed (ensemble) state, respectively. This choice is such that Klyachko's conditions in the $(4e, 3o)$ model system are satisfied for both $w = 0.0$ and $w = 0.5$, whereas in the $(4e, 4o)$ case, these conditions are satisfied only for $w = 0.0$ (see Table S1 in the SI for the complete list of inequalities). Table 2 shows our results for the

https://doi.org/10.1021/acs.jctc.5c01788
J. Chem. Theory Comput. 2026, 22, 399−406

Table 2. Converged $\mathcal{D}_{min}$ from the Pure and Ensemble ADAPT-VQA for 4-Electron Model Systems for 1-RDMs, Along with the 1-RDMs Eigenvalues, and the Number of Klyachko's Pure *N*-Representability Inequalities That is Fulfilled in Each Case, N_{ineq} (Out of a Total of 15 for This Model)

	Model system			
	(4*e*, 3*o*)		(4*e*, 4*o*)	
1-RDM eigenvalues	w = 0.0	w = 0.5	w = 0.0	w = 0.5
λ_1	1.000	1.000	1.000	1.000
λ_2	1.000	1.000	1.000	1.000
λ_3	1.000	0.500	1.000	1.000
λ_4	1.000	0.500	1.000	0.500
λ_5	0.000	0.500	0.000	0.500
λ_6	0.000	0.500	0.000	0.000
λ_7			0.000	0.000
λ_8			0.000	0.000
N_{ineq}	15	15	15	7
ADAPT-VQA	$\mathcal{D}_{min}$			
Pure	0.0	4.89×10^{-9}	0.0	1.25×10^{-1}
Ensemble	0.0	4.89×10^{-9}	0.0	2.45×10^{-9}

1-RDM of the (4*e*, 3*o*) and (4*e*, 4*o*) model systems for w = 0.0 and w = 0.5. In all cases, the initial state is taken as ρ_1 for the pure case, or its purification for the ensemble case. For the (4*e*, 3*o*) model system, the pure and ensemble ADAPT-VQA yield converged $\mathcal{D}_{min}$ that are numerically zero for both w values, indicating that there exists pure states that are compatible with the target 1-RDMs. This is consistent with the satisfaction of all Klyachko's conditions, as shown in Table 2. For the (4*e*, 4*o*) model system, on the other hand, both the pure and ensemble ADAPT-VQAs yield converged $\mathcal{D}_{min} \approx 0$ for w = 0.0, while for w = 0.5 (for which Klyachko's conditions are not fulfilled), $\mathcal{D}_{min}$ approaches zero only for the ensemble algorithm. This highlights the ability of the algorithms to discern the pure or ensemble *N*-representability nature of 1-RDMs. Table 2 also reports the number of Klyachko's inequalities that are satisfied for each case. We note that all targets are identified as ensemble *N*-representable by the ensemble ADAPT-VQA, in agreement with the fulfillment of Coleman's ensemble *N*-representability conditions (1-RDM eigenvalues between 0 and 1, and tracing to the number of electrons).[4]

Next, we extend the analysis to 2-RDMs. While a set of necessary pure *N*-representability conditions has been reported for 2-RDMs,[44] the complete set of necessary and sufficient pure *N*-representability conditions remains unknown. Our ADAPT-VQA can be used to numerically decide the pure or ensemble *N*-representability of 2-RDMs. To highlight this, we analyze the *N*-representability of 2-RDMs for the (4*e*, 3*o*) and (4*e*, 4*o*) model systems. Our results are summarized in Table 3. For these model systems, the algorithm identifies all the 2-RDMs as ensemble *N*-representable, but only the cases corresponding to w = 0.0 are identified as pure *N*-representable, as expected. This brings an interesting question: Can the method be used to detect if an ensemble *N*-representable *p*-RDM would contract to a pure *N*-representable *q*-RDM ($q < p$)? To answer this question, we build target RDMs for a (4*e*, 4*o*) model system from an ensemble state as linear combination of two pure states (eq 10 with w = 0.5), which are in turn constructed as shown in Table 4. These

Table 4. Singly- (1), Doubly- (2), and Triply- (3) Spin-Orbital-Substituted States Used to Construct the Target RDMs for the (4*e*, 4*o*) Model System

Substitution	ρ_1	ρ_2
1	$\|1^\alpha\ 1^\beta\ 2^\alpha\ 2^\beta\rangle$	$\|1^\alpha\ 1^\beta\ 3^\alpha\ 2^\beta\rangle$
2	$\|1^\alpha\ 1^\beta\ 2^\alpha\ 2^\beta\rangle$	$\|1^\alpha\ 1^\beta\ 3^\alpha\ 3^\beta\rangle$
3	$\|1^\alpha\ 1^\beta\ 2^\alpha\ 2^\beta\rangle$	$\|1^\alpha\ 3^\beta\ 4^\alpha\ 4^\beta\rangle$

states are chosen so that they differ in one, two, or three spin−orbitals. A summary of the results is shown in Table 5. For the case of triple substitution, the 1-RDM and the 2-RDM can be also obtained from a wave function (a linear combination of those reported in Table 4), and thus they are both pure and ensemble *N*-representable. This indicates that the *N*-electron state that generated these RDMs cannot be uniquely determined solely from them. Thus, $\mathcal{D}_{min}$ is expected to approach zero as the pure and ensemble algorithms evolve. The numerical results shown in Table 5 confirm that the ADAPT-VQA yields the expected outcomes. For the doubly substituted case, only the pure algorithm yields $\mathcal{D}_{min} \neq 0$ for the 2-RDM, showing that indeed this matrix corresponds to an ensemble state, while its contraction leads to a 1-RDM that can be identified as pure *N*-representable. For completeness, Table 5 shows the results for the single substitution case, indicating that neither the target 1-RDM nor the target 2-RDM can be obtained from a pure state. It is important to emphasize that, although the 1- and 2-RDMs are constructed from an ensemble state, the pure algorithm is able to find a compatible wave function that yields the same RDMs (provided that $\mathcal{D}_{min} \to 0$), highlighting its potential use in quantum tomography.[61]

So far we have tested our ADAPT-VQA with *N*-representable RDMs as targets. To test the ensemble algorithm with cases where the *N*-representability is violated, we have incorporated numerical noise to RDMs, ${}^p\rho$, using

$$ {}^p\rho_{target}(\varepsilon) = {}^p\rho + \varepsilon R \tag{11} $$

where R is a matrix of random numbers taken from a uniform probability distribution in $[-1, 1]$ and ε is in the interval $[0, 0.1]$. In eq 11, ${}^p\rho$ is constructed according to eq 10 with w = 0.5 and ρ_1 and ρ_2 given in Table 1. The values of ε are chosen so that the resulting noise produces noticeably *N*-representability defects on ${}^p\rho_{target}(\varepsilon)$. Thus, the algorithm should evolve

Table 3. Converged $\mathcal{D}_{min}$ from the Pure and Ensemble ADAPT-VQA for the (4*e*, 3*o*) and (4*e*, 4*o*) Model Systems for 2-RDMs

	$\mathcal{D}_{min}$			
	(4*e*, 3*o*)		(4*e*, 4*o*)	
Algorithm	w = 0.0	w = 0.5	w = 0.0	w = 0.5
Pure	0.0	2.00	0.0	4.25
Ensemble	1.07×10^{-14}	3.11×10^{-12}	1.07×10^{-14}	1.07×10^{-14}

https://doi.org/10.1021/acs.jctc.5c01788
J. Chem. Theory Comput. 2026, 22, 399−406

Table 5. Converged $\mathcal{D}_{min}$ from the Pure and Ensemble ADAPT-VQA for the (4e, 4o) Model System for 1- and 2-RDMs with w = 0.5. The Targets are the (Ensemble) Reduced Density Matrices Corresponding to the States Constructed from Multiple Substitutions as Shown in Table 4

	$\mathcal{D}_{min}$			
	1-RDM		2-RDM	
	Algorithm			
Substitution	Pure	Ensemble	Pure	Ensemble
1	1.25×10^{-1}	2.45×10^{-9}	4.25	1.07×10^{-14}
2	4.89×10^{-9}	4.89×10^{-9}	2.00	9.66×10^{-9}
3	2.45×10^{-9}	2.45×10^{-9}	1.42×10^{-14}	2.77×10^{-8}

the initial RDM toward the target up to a certain limit, depending on the strength of the noise. Larger noise strengths should lead to larger $\mathcal{D}_{min}$, while a noiseless target should converge $\mathcal{D}_{min} \to 0$ as previously shown. Table 6 shows the converged $\mathcal{D}_{min}$ for ${}^1\rho_{target}(\varepsilon)$ and ${}^2\rho_{target}(\varepsilon)$ corresponding to the (4e, 4o) model system for different noise strengths. The converged $\mathcal{D}_{min}$ in Table 6 can then be considered as a numerical measure of the violation of the ensemble N-representability. These results are in line with the findings in ref 32 for the pure ADAPT-VQA when considering systematic violations of N-representability conditions. This emphasizes applications for the ADAPT-VQA: It can be used not only to determine the ensemble N-representability of an alleged p-RDM, but also to construct an ensemble p-RDM (the evolved RDM) that is closest to the target ${}^p\rho_{target}$.

Table 6. Converged $\mathcal{D}_{min}$ from the Ensemble ADAPT-VQA for the 1- and 2-RDMs in the (4e, 4o) Model System[a]

	$\mathcal{D}_{min}$	
ε	1-RDM	2-RDM
0.0	2.45×10^{-9}	1.07×10^{-14}
10^{-2}	2.02×10^{-3}	1.38×10^{-1}
10^{-1}	2.19×10^{-1}	1.33×10^{1}

[a]The targets are constructed by adding random noise of strength ε to the reduced density matrices (see text for details).

Molecular Systems at Finite Temperature. We next assess the usability of the ensemble ADAPT-VQA for H_2 and linear H_3 molecular systems at a finite temperature. In this case, the p-RDMs are constructed from their canonical ensemble thermal states at temperature T,

$$\rho = Z^{-1} \sum_i e^{-E_i/k_B T} \rho_i \tag{12}$$

where k_B is the Boltzmann constant, and the canonical partition function Z is given by

$$Z = \sum_i e^{-E_i/k_B T} \tag{13}$$

In eq 12, E_i and ρ_i are the eigenenergies and eigenstates of the electronic Hamiltonian H, which can be written in the second quantization formalism as[62]

$$\hat{H} = \sum_{ij} \langle i|h|j\rangle \hat{a}_i^\dagger \hat{a}_j + \frac{1}{4} \sum_{ijkl} \langle ij|v|kl\rangle \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_l \hat{a}_k \tag{14}$$

where $\langle i|h|j\rangle$ and $\langle ij|v|kl\rangle$ are the standard one- and two-electron antisymmetrized integrals, respectively.

We consider both molecular systems at two nuclear configurations: close to equilibrium (R_{HH} = 0.75 Å) and stretched (R_{HH} = 1.5 Å). In all cases $k_B T$ is the energy gap between the ground and first excited states. With this choice, the stretched configuration presents a thermal distribution with larger weights for the lower energy states than that of the equilibrium configuration. Using the ensemble RDMs corresponding to these thermally weighted states, we construct target matrices by adding random noise of strength ε as described above (see eq 11). We observe that for H_2, the 2-RDM is not a reduced state of the system. In all cases, the initial state has been constructed considering eq 4, with $|\phi_0\rangle$ the Hartree–Fock ground state. In Table 7 we show the converged $\mathcal{D}_{min}$ for three values of ε. The results should serve as an indication of what to expect for the ensemble ADAPT-VQA for physical systems when the target matrices deviate from ideal ensemble N-representability. For example, when this deviation increases, as measured by the parameter ε, $\mathcal{D}_{min}$ also increases to values of $\sim 10^{-2}$ and $\sim 10^{0}$ for the 1- and 2-RDM for ε = 0.1, respectively. We note that this observation holds for both nuclear configurations, indicating that the converged $\mathcal{D}_{min}$ is more sensitive to the added noise than to the correlated characteristic of the underlying noiseless reduced state.

Table 7. Converged $\mathcal{D}_{min}$ from the Ensemble ADAPT-VQA for the Equilibrium and Stretched H_2 and Linear H_3 molecules[a]

	$\mathcal{D}_{min}$			
	H_2		H_3	
ε	1-RDM	2-RDM	1-RDM	2-RDM
R_{HH} = 0.75 Å				
0.0	0.0	4.95×10^{-9}	4.45×10^{-9}	1.98×10^{-5}
10^{-2}	3.11×10^{-4}	8.12×10^{-3}	1.08×10^{-3}	4.24×10^{-2}
10^{-1}	3.55×10^{-2}	7.71×10^{-1}	9.27×10^{-2}	4.08
R_{HH} = 1.5 Å				
0.0	0.0	1.76×10^{-7}	4.11×10^{-10}	4.73×10^{-5}
10^{-2}	4.08×10^{-4}	7.67×10^{-3}	9.40×10^{-4}	4.44×10^{-2}
10^{-1}	4.95×10^{-2}	7.98×10^{-1}	6.47×10^{-2}	4.20

[a]The targets are constructed by adding random noise of strength ε to the RDMs corresponding to canonical ensemble thermal states (see text for details).

SUMMARY

We have proposed and assessed a practical framework for determining the ensemble N-representability of an (alleged) p-body RDM. To this end, we employ a purification scheme that

https://doi.org/10.1021/acs.jctc.5c01788
J. Chem. Theory Comput. 2026, 22, 399−406

embeds an ensemble state into a pure state defined on an extended Hilbert space, in a way that the reduced density matrices of the purified state reproduce those of the original ensemble. We then utilize a recently reported unitary-evolution algorithm for pure RDMs to iteratively apply variational unitaries to an initial purified state. The algorithm effectively minimizes the distance between the corresponding p-body reduced density matrix and a specified target p-body matrix, alleged to be a proper ensemble p-RDM. This methodology can be used for both, correcting the lack of ensemble N-representability of target matrices and reconstructing a quantum-state from the corrected targets, offering a route for p-RDM refinement. Moreover, the proposed algorithm is compatible with quantum computers.

We have validated the algorithm with numerical simulations on systems of two, three, and four electrons in both, model problems and molecular examples. For model systems of four electrons in three and four orbitals, we have assessed the effectiveness of the algorithm to decide on the pure or ensemble nature of 1-RDMs, and compared against Klyachko's pure N-representability conditions. For 2-RDMs, where the sufficient pure N-representability conditions are unknown, our algorithm offers a practical route for dealing with this problem. We have also considered the capability of the ADAPT-VQA to deal with cases where the target matrices may not be N-representable. To this end, we have generated target matrices by artificially breaking the N-representability of 1- and 2-RDMs in a model system, and in molecular H_2 and H_3 at finite temperature. Overall, the numerical results show that the proposed algorithm is effectively able to detect the type of N-representability (pure or ensemble) of a target matrix, or the lack of it, as well as provide a closest RDM to a given non-N-representable target matrix and the corresponding (pure or purified) state.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jctc.5c01788.

Klyachko's pure N-representability inequalities for the $(4e, 3o)$ and $(4e, 4o)$ model systems, and the number of iterations required to achieve convergence for the various systems in this work (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

Juan E. Peralta − *Department of Physics, Central Michigan University, Mount Pleasant, Michigan 48859, United States;* orcid.org/0000-0003-2849-8472; Email: juan.peralta@cmich.edu

Diego R. Alcoba − *Universidad de Buenos Aires, Facultad de Ciencias Exactas Y Naturales, Departamento de Física, Buenos Aires 1428, Argentina; CONICET - Universidad de Buenos Aires, Instituto de Física de Buenos Aires (IFIBA), Buenos Aires 1428, Argentina;* orcid.org/0000-0001-5165-1127; Email: dalcoba@df.uba.ar

Gustavo E. Scuseria − *Department of Chemistry, Rice University, Houston, Texas 77005-1892, United States; Department of Physics and Astronomy, Rice University, Houston, Texas 77005-1892, United States;* Email: guscus@rice.edu

Authors

Ofelia B. Oña − *Instituto de Investigaciones Fisicoquímicas Teóricas Y Aplicadas, Universidad Nacional de La Plata, Consejo Nacional de Investigaciones Científicas Y Técnicas, La Plata 1900, Argentina;* orcid.org/0000-0002-2482-5109

Gustavo E. Massaccesi − *Departamento de Ciencias Exactas, Ciclo Básico Común, Universidad de Buenos Aires, Buenos Aires 1428, Argentina; Instituto de Investigaciones Matemáticas "Luis A. Santaló" (IMAS), Consejo Nacional de Investigaciones Científicas Y Técnicas, Universidad de Buenos Aires, Buenos Aires 1428, Argentina;* orcid.org/0000-0001-7390-5255

Pablo Capuzzi − *Universidad de Buenos Aires, Facultad de Ciencias Exactas Y Naturales, Departamento de Física, Buenos Aires 1428, Argentina; CONICET - Universidad de Buenos Aires, Instituto de Física de Buenos Aires (IFIBA), Buenos Aires 1428, Argentina;* orcid.org/0000-0003-1271-672X

Luis Lain − *Department of Physical Chemistry, Faculty of Science and Technology, University of the Basque Country, Bilbao E-48080, Spain;* orcid.org/0000-0002-7260-049X

Alicia Torre − *Department of Physical Chemistry, Faculty of Science and Technology, University of the Basque Country, Bilbao E-48080, Spain;* orcid.org/0000-0002-5681-7074

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.jctc.5c01788

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

O.B.O., G.E.M., P.C., and D.R.A. acknowledge the financial support from the Consejo Nacional de Investigaciones Científicas y Técnicas (grant No. PIP KE3 11220200100467CO and PIP KE3 11220210100821CO). O.B.O., G.E.M., P.C., and D.R.A. also acknowledge support from the Universidad de Buenos Aires (grant No. 20020190100214BA and 20020220100069BA) and the Agencia Nacional de Promoción Científica y Tecnológica (grant No. PICT-201-0381). J.E.P. acknowledges support from NSF award number DMR-2318872. G.E.S. is a Welch Foundation Chair (C-0036), and his work was supported by the U.S. Department of Energy under Award No. DE-SC0019374.

■ REFERENCES

(1) National Research Council. *Mathematical Challenges from Theoretical/Computational Chemistry*; The National Academies Press: Washington, DC, 1995.

(2) Mazziotti, D. *Reduced-Density-Matrix Mechanics: with Application to Many-Electron Atoms and Molecules*; John Wiley & Sons, Inc.: Hoboken, NJ, 2007; Vol. *134*, pp. 165−203.

(3) Coleman, A. J.; Yukalov, V. I. *Reduced Density Matrices: coulson's Challenge*; Springer: Berlin Heidelberg. 2000.

(4) Coleman, A. J. Structure of Fermion Density Matrices. *Rev. Mod. Phys.* **1963**, *35*, 668−686.

(5) Garrod, C.; Percus, J. K. Reduction of the N-Particle Variational Problem. *J. Math. Phys.* **1964**, *5*, 1756−1776.

(6) Kummer, H. N-Representability Problem for Reduced Density Matrices. *J. Math. Phys.* **1967**, *8*, 2063−2081.

(7) Erdahl, R. M. Representability. *Int. J. Quantum Chem.* **1978**, *13*, 697−718.

(8) Erdahl, R. M.; Smith, V. H. *Density Matrices and Density Functionals: proceedings of the A. John Coleman Symposium*; Springer Netherlands, 1987.
(9) Mazziotti, D. A. Structure of Fermionic Density Matrices: Complete *N*-Representability Conditions. *Phys. Rev. Lett.* **2012**, *108*, 263002.
(10) DePrince, A. E. Variational determination of the two-electron reduced density matrix: A tutorial review. *WIREs Comput. Mol. Sci.* **2024**, *14* (1), No. e1702.
(11) Kryachko, E. S.; Ludeña, E. V. Proto, A. N.; Aliaga, J. L. *Condensed Matter Theories*; Springer US: Boston, MA, 1992; pp. 229−241
(12) Parr, R. G.; Yang, W. *Density-Functional Theory of Atoms and Molecules*; Oxford University Press: USA, 1994.
(13) Piris, M. Angilella, G.; Amovilli, C. *In Many-body Approaches at Different Scales: A Tribute to Norman H. March on the Occasion of his 90th Birthday*; Springer International Publishing: Cham, 2018; pp. 261−278
(14) Liu, Y.-K.; Christandl, M.; Verstraete, F. Quantum Computational Complexity of the *N*-Representability Problem: QMA Complete. *Phys. Rev. Lett.* **2007**, *98*, 110503.
(15) Poelmans, W.; Van Raemdonck, M.; Verstichel, B.; De Baerdemacker, S.; Torre, A.; Lain, L.; Massaccesi, G. E.; Alcoba, D. R.; Bultinck, P.; Van Neck, D. Variational Optimization of the Second-Order Density Matrix Corresponding to a Seniority-Zero Configuration Interaction Wave Function. *J. Chem. Theory Comput.* **2015**, *11*, 4064−4076.
(16) Alcoba, D. R.; Torre, A.; Lain, L.; Massaccesi, G. E.; Oña, O. B.; Honoré, E. M.; Poelmans, W.; Van Neck, D.; Bultinck, P.; De Baerdemacker, S. Direct variational determination of the two-electron reduced density matrix for doubly occupied-configuration-interaction wave functions: The influence of three-index N-representability conditions. *J. Chem. Phys.* **2018**, *148*, 024105.
(17) Alcoba, D. R.; Capuzzi, P.; Rubio-García, A.; Dukelsky, J.; Massaccesi, G. E.; Oña, O. B.; Torre, A.; Lain, L. Variational reduced density matrix method in the doubly occupied configuration interaction space using three-particle N-representability conditions. *J. Chem. Phys.* **2018**, *149* (19), 194105.
(18) Alcoba, D. R.; Torre, A.; Lain, L.; Oña, O. B.; Ríos, E.; Massaccesi, G. E. Incorporating dynamic correlation into the variational determination method of the second-order reduced density matrix in the doubly occupied configuration interaction space. *Int. J. Quantum Chem.* **2020**, *120*, No. e26256.
(19) Mazziotti, D. A. Dual-cone variational calculation of the two-electron reduced density matrix. *Phys. Rev. A* **2020**, *102*, 052819.
(20) Mazziotti, D. A. Quantum Many-Body Theory from a Solution of the *N*-Representability Problem. *Phys. Rev. Lett.* **2023**, *130*, 153001.
(21) Klyachko, A. A. Quantum marginal problem and N-representability. *J. Phys.: conf. Ser.* **2006**, *36*, 72.
(22) Altunbulak, M.; Klyachko, A. The Pauli Principle Revisited. *Commun. Math. Phys.* **2008**, *282*, 287−322.
(23) Coleman, A. J. Reduced density operators and the N-particle problem. *Int. J. Quantum Chem.* **1978**, *13*, 67−82.
(24) Schilling, C.; Gross, D.; Christandl, M. Pinning of Fermionic Occupation Numbers. *Phys. Rev. Lett.* **2013**, *110*, 040404.
(25) Chakraborty, R.; Mazziotti, D. A. Generalized Pauli conditions on the spectra of one-electron reduced density matrices of atoms and molecules. *Phys. Rev. A* **2014**, *89*, 042505.
(26) Theophilou, I.; Lathiotakis, N. N.; Marques, M. A. L.; Helbig, N. Generalized Pauli constraints in reduced density matrix functional theory. *J. Chem. Phys.* **2015**, *142*, 154108.
(27) Schilling, C. Communication: Relating the pure and ensemble density matrix functional. *J. Chem. Phys.* **2018**, *149*, 231102.
(28) Smart, S. E.; Schuster, D. I.; Mazziotti, D. A. Experimental data from a quantum computer verifies the generalized Pauli exclusion principle. *Commun. Phys.* **2019**, *2*, 11.
(29) Boyn, J.-N.; Mazziotti, D. A. Sparse non-orthogonal wave function expansions from the extension of the generalized Pauli constraints to the two-electron reduced density matrix. *J. Chem. Phys.* **2019**, *150*, 144102.
(30) Avdic, I.; Sager-Smith, L. M.; Ghosh, I.; Wedig, O. C.; Higgins, J. S.; Engel, G. S.; Mazziotti, D. A. Quantum sensing using multiqubit quantum systems and the Pauli polytope. *Phys. Rev. Res.* **2023**, *5*, 043097.
(31) Benavides-Riveros, C. L.; Gracia-Bondía, J. M.; Springborg, M. Quasipinning and entanglement in the lithium isoelectronic series. *Phys. Rev. A* **2013**, *88*, 022508.
(32) Massaccesi, G. E.; Oña, O. B.; Capuzzi, P.; Melo, J. I.; Lain, L.; Torre, A.; Peralta, J. E.; Alcoba, D. R.; Scuseria, G. E. Determining the N-Representability of a Reduced Density Matrix via Unitary Evolution and Stochastic Sampling. *J. Chem. Theory Comput.* **2024**, *20*, 9968−9976.
(33) Grimsley, H. R.; Economou, S. E.; Barnes, E.; Mayhall, N. J. An adaptive variational algorithm for exact molecular simulations on a quantum computer. *Nat. Commun.* **2019**, *10*, 3007.
(34) Smart, S. E.; Mazziotti, D. A. Quantum Solver of Contracted Eigenvalue Equations for Scalable Molecular Simulations on Quantum Computing Devices. *Phys. Rev. Lett.* **2021**, *126*, 070504.
(35) Warren, S.; Wang, Y.; Benavides-Riveros, C. L.; Mazziotti, D. A. Exact Ansatz of Fermion-Boson Systems for a Quantum Device. *Phys. Rev. Lett.* **2024**, *133*, 080202.
(36) Yordanov, Y. S.; Armaos, V.; Barnes, C. H. W.; Arvidsson-Shukur, D. R. M. Qubit-excitation-based adaptive variational quantum eigensolver. *Commun. Phys.* **2021**, *4*, 228.
(37) Tang, H. L.; Shkolnikov, V.; Barron, G. S.; Grimsley, H. R.; Mayhall, N. J.; Barnes, E.; Economou, S. E. Qubit-ADAPT-VQE: An Adaptive Algorithm for Constructing Hardware-Efficient Ansätze on a Quantum Processor. *PRX Quantum.* **2021**, *2*, 020310.
(38) Liu, H.; Low, G. H.; Steiger, D. S.; Häner, T.; Reiher, M.; Troyer, M. Prospects of quantum computing for molecular sciences. *Mater. Theory* **2022**, *6*, 11.
(39) Stein, S.; Wiebe, N.; Ding, Y.; Bo, P.; Kowalski, K.; Baker, N.; Ang, J.; Li, A. EQC: ensembled quantum computing for variational quantum algorithms. *arXiv* **2021**.
(40) Ziems, K. M.; Kjellgren, E. R.; Reinholdt, P.; Jensen, P. W. K.; Sauer, S. P. A.; Kongsted, J.; Coriani, S. Which Options Exist for NISQ-Friendly Linear Response Formulations? *J. Chem. Theory Comput.* **2024**, *20*, 3551−3565.
(41) Vaquero-Sabater, N.; Carreras, A.; Orús, R.; Mayhall, N. J.; Casanova, D. Physically Motivated Improvements of Variational Quantum Eigensolvers. *J. Chem. Theory Comput.* **2024**, *20*, 5133−5144.
(42) Fedorov, D. A.; Peng, B.; Govind, N.; Alexeev, Y. VQE method: a short survey and recent developments. *Mater. Theory* **2022**, *6*, 2.
(43) Bharti, K.; Cervera-Lierta, A.; Kyaw, T. H.; Haug, T.; Alperin-Lea, S.; Anand, A.; Degroote, M.; Heimonen, H.; Kottmann, J. S.; Menke, T.; Mok, W.-K.; Sim, S.; Kwek, L.-C.; Aspuru-Guzik, A. Noisy intermediate-scale quantum algorithms. *Rev. Mod. Phys.* **2022**, *94*, 015004.
(44) Mazziotti, D. A. Pure-*N*-representability conditions of two-fermion reduced density matrices. *Phys. Rev. A* **2016**, *94*, 032516.
(45) Nielsen, M. A.; Chuang, I. L. *Quantum Computation and Quantum Information*; Cambridge University Press: Cambridge, 2000; pp. 110−111.
(46) Hughston, L. P.; Jozsa, R.; Wootters, W. K. A complete classification of quantum ensembles having a given density matrix. *Phys. Lett. A* **1993**, *183*, 14−18.
(47) Harsha, G.; Henderson, T. M.; Scuseria, G. E. Thermofield theory for finite-temperature quantum chemistry. *arXiv* **2019**.
(48) Harsha, G.; Henderson, T. M.; Scuseria, G. E. Wave function methods for canonical ensemble thermal averages in correlated many-fermion systems. *J. Chem. Phys.* **2020**, *153*, 124115.
(49) Harsha, G.; Henderson, T. M.; Scuseria, G. E. Thermofield Theory for Finite-Temperature Electronic Structure. *J. Phys. Chem. A* **2023**, *127*, 3063−3071.
(50) Kirkpatrick, K. The Schrödinger-HJW Theorem. *Found. Phys. Lett.* **2006**, *19*, 95−102.

(51) Massaccesi, G. E.; Capuzzi, P.; Oña, O. B.; Lain, L.; Torre, A.; Peralta, J. E.; Alcoba, D. R. Determining the N-representability of transition reduced density matrices. *J. Chem. Phys.* **2025**, *163*, 034119.
(52) Mazziotti, D. A. Anti-Hermitian part of the contracted Schrödinger equation for the direct calculation of two-electron reduced density matrices. *Phys. Rev. A* **2007**, *75*, 022505.
(53) O'Malley, P. J. J.; et al. Scalable Quantum Simulation of Molecular Energies. *Phys. Rev. X* **2016**, *6*, 031007.
(54) Barkoutsos, P. K.; Gonthier, J. F.; Sokolov, I.; Moll, N.; Salis, G.; Fuhrer, A.; Ganzhorn, M.; Egger, D. J.; Troyer, M.; Mezzacapo, A.; Filipp, S.; Tavernelli, I. Quantum algorithms for electronic structure calculations: Particle-hole Hamiltonian and optimized wave-function expansions. *Phys. Rev. A* **2018**, *98*, 022322.
(55) Evangelista, F. A.; Chan, G. K.-L.; Scuseria, G. E. Exact parameterization of fermionic wave functions via unitary coupled cluster theory. *J. Chem. Phys.* **2019**, *151*, 244112.
(56) Jordan, P.; Wigner, E. P. Wightman, A. S. *In The Collected Works of Eugene Paul Wigner: part A: The Scientific Papers*; Springer: Berlin Heidelberg, 1993; pp. 109−129
(57) Tilly, J.; Chen, H.; Cao, S.; Picozzi, D.; Setia, K.; Li, Y.; Grant, E.; Wossnig, L.; Rungger, I.; Booth, G. H.; Tennyson, J. The Variational Quantum Eigensolver: A review of methods and best practices. *Phys. Rep.* **2022**, *986*, 1−128.
(58) McClean, J. R.; et al. OpenFermion: the electronic structure package for quantum computers. *Quantum Sci. Technol.* **2020**, *5*, 034014.
(59) Sun, Q.; Berkelbach, T. C.; Blunt, N. S.; Booth, G. H.; Guo, S.; Li, Z.; Liu, J.; McClain, J. D.; Sayfutyarova, E. R.; Sharma, S.; Wouters, S.; Chan, G. K.-L. PySCF: the Python-based simulations of chemistry framework. *WIREs Comput. Mol. Sci.* **2018**, *8*, No. e1340.
(60) Sun, Q.; Zhang, X.; Banerjee, S.; Bao, P.; Barbry, M.; Blunt, N. S.; Bogdanov, N. A.; Booth, G. H.; Chen, J.; Cui, Z.-H.; Eriksen, J. J.; et al. Recent developments in the PySCF program package. *J. Chem. Phys.* **2020**, *153* (2), 024109.
(61) Xin, T.; Lu, D.; Klassen, J.; Yu, N.; Ji, Z.; Chen, J.; Ma, X.; Long, G.; Zeng, B.; Laflamme, R. Quantum State Tomography via Reduced Density Matrices. *Phys. Rev. Lett.* **2017**, *118*, 020401.
(62) Surján, P. R. *Second Quantized Approach to Quantum Chemistry*; Springer: Berlin, Heidelberg, 1989.

https://doi.org/10.1021/acs.jctc.5c01788
J. Chem. Theory Comput. 2026, 22, 399−406