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Enhanced Constraints for Accurate Lower Bounds on Many-electron Quantum Energies from Variational 2-Electron Reduced Density Matrix Theory

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A central challenge of physics is the computation of strongly correlated quantum systems. The past 10 years have witnessed the development and application of the variational calculation of the two-electron reduced density matrix (2-RDM) without the wave function. In this Letter we present an orders-of-magnitude improvement in the accuracy of 2-RDM calculations without an increase in their computational cost. The advance is based on a low-rank, dual formulation of an important constraint on the 2-RDM, the T2 condition. Calculations are presented for metallic chains and a cadmium selenide dimer. The low-scaling T2 condition will have significant applications in atomic and molecular, condensed-matter, and nuclear physics.

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Strong electron correlation in a quantum system occurs when two or more electronic configurations contribute significantly and nearly equally to its wave function [1–3]. In many physical systems the number of orbitals participating in the strong correlation increases linearly with system size, which causes the number of significant electron configurations in the wave function to increase *exponentially*. Approaches to strong correlation often employ sophisticated parameterizations of the wave function as in the Bardeen-Cooper-Schrieffer ansatz for superconductivity [4–6] or the general formalism of matrix product states [7]. Notwithstanding, the complexity of strongly correlated electrons can also be reduced by exploiting indistinguishability of the electrons together with their pairwise interactions to express the ground-state energy as a linear functional of only the two-electron reduced density matrix (2-RDM) [8, 9]. In a variational calculation the 2-RDM must be constrained to derive from the integration of an N -electron density matrix; the constraints, known as N -representability conditions [10–15] can be systematically arranged in a hierarchy where each level of the hierarchy yields an increasingly tighter lower bound on the ground-state energy. Applications of the second level of the hierarchy to strongly correlated systems, however, have been significantly limited by the computational complexity of the conditions. In this Letter the computational cost of these conditions is dramatically reduced through a dual formulation with rank reduction, realizing more accurate and efficient 2-RDM calculations of strongly correlated quantum systems.

The first level of N -representability conditions, known as the 2-positivity or DQG conditions [11, 14–18], have been applied to treat strong electron correlation in many molecular applications including the metal-to-insulator transition in molecular chains [19–21], the emergence of poly-radical character in one- and two-dimensional polyaromatic hydrocarbons [22–24], conical intersections and efficient energy transfer in firefly bioluminescence [25], and the role of entangled electrons in the re-

duction of a vanadium-oxo transition-metal complex [26] as well as applications to quantum dots [27] and phase transitions [28, 29]. Nevertheless, the ground-state energy and 2-RDM from the DQG conditions can be significantly improved by adding constraints from the second level of N -representability conditions, known as the (2,3)-positivity conditions, including the T1 and T2 conditions [13, 15, 30, 31]. Such improvement has been observed consistently in atoms and molecules [24, 30–33] as well as spin systems including Erdahl [34, 35], Hubbard [36–39], Ising [29], and Lipkin [28] spin models. Unlike the DQG conditions which have a computational scaling of r^4 and r^6 in memory and floating-point operations where r is the number of orbitals, the T1 and T2 conditions have a computational scaling of r^6 and r^9 , which severely restricts their application to large r . In this Letter, through two advances (*i*) a dual formulation of the variational 2-RDM method as well as (*ii*) a rank reduction exploiting the locality of the Coulomb interaction, the T2 condition is implemented with the same computational scaling as DQG. Applications are made to hydrogen chains and a newly discovered cadmium selenide dimer that are not treatable by conventional calculations of the wave function.

Because electrons are indistinguishable with pairwise interactions, the energy as a function of the wave function

$$E[\Psi] = \int \hat{H}\Psi(1, 2, \dots, N)\Psi^*(\bar{1}, \bar{2}, \dots, \bar{N})d1d2\dots dN \quad (1)$$

can be replaced by the energy as a function of the 2-RDM [1, 2, 8, 9]

$$E[{}^2D] = \int {}^2\hat{K} {}^2D(12; \bar{1}\bar{2})d1d2, \quad (2)$$

where ${}^2\hat{K}$ is the reduced Hamiltonian operator

$${}^2\hat{K} = -\frac{N}{2} \sum_{i=1}^2 \left(\frac{1}{2} \hat{\nabla}_i^2 + \sum_k \frac{Z_k}{r_{ik}} \right) + \frac{N(N-1)}{2} \frac{1}{r_{12}} \quad (3)$$

and

$${}^2D(12; \bar{1}\bar{2}) = \int \Psi(1, 2, \dots, N) \Psi^*(\bar{1}, \bar{2}, \dots, N) d3\dots dN. \quad (4)$$

The symbol Z_k denotes the nuclear charge of k^{th} atom, r_{ik} is the distance between the i^{th} electron and the k^{th} nucleus, and r_{12} is the distance between electrons 1 and 2. An N -electron density matrix must be (i) Hermitian, (ii) normalized, (iii) antisymmetric upon exchange of a pair of electrons, and (iv) positive semidefinite. The 2-RDM in Eq. (2) must obey these fundamental requirements for a density matrix as well as N -representability conditions that constrain the 2-RDM to represent an N -electron density matrix.

In a finite basis set of r spin orbitals the variational calculation of the ground-state energy as a 2-RDM functional, constrained by the 2-positivity (DQG) conditions [11, 14–17], can be expressed as

$$\min \text{Tr}({}^2K {}^2D) \quad (5)$$

$$\text{such that } {}^2D \succeq 0 \quad (6)$$

$${}^2Q \succeq 0 \quad (7)$$

$${}^2G \succeq 0 \quad (8)$$

$$\text{Tr}({}^2D) = 1 \quad (9)$$

in which the elements of the 2D , 2Q , and 2G matrices are related by linear equations, 2K is the matrix representation of reduced Hamiltonian operator in Eq. (3), and $M \succeq 0$ indicates that the matrix M is constrained to be positive semidefinite. A matrix is *positive semidefinite* if and only if its eigenvalues are nonnegative. The D, Q, and G conditions restrict the probability distributions of two particles, two holes, and a particle-hole pair to be nonnegative, respectively. Variational calculation of the 2-RDM with the 2-positivity (DQG) conditions can be solved by first-order semidefinite programming [19, 21] at a computational scaling of r^6 in floating-point operations and r^4 in memory storage.

The lower bound on the ground-state energy from the 2-positivity conditions can be improved by adding conditions from the (2,3)-positivity conditions such as the T1 and the T2 conditions [13, 15, 30, 31]. The T2 condition can be expressed as

$${}^2T \succeq 0 \quad (10)$$

where

$${}^2T_{pqrs}^{ijk} = \int \left({}^3\hat{E}_{pqrs}^{ijk} + {}^3\hat{F}_{pqrs}^{ijk} \right) {}^2D(12; \bar{1}\bar{2}) d1d2 \quad (11)$$

with

$${}^3\hat{E}_{pqrs}^{ijk} = \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_k \hat{a}_s^\dagger \hat{a}_q \hat{a}_p \quad (12)$$

$${}^3\hat{F}_{pqrs}^{ijk} = \hat{a}_s^\dagger \hat{a}_q \hat{a}_p \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_k. \quad (13)$$

The creation \hat{a}_i^\dagger and annihilation \hat{a}_i operators create and annihilate an electron in the spin orbital i . The ${}^3\hat{E}$ and

${}^3\hat{F}$ operators correspond to metric matrices that enforce non-negativity of the probability distribution of two particles and one hole and the probabilities distribution of two holes and one particle, respectively. The sum of these two operators, however, cancels the 3-body terms, generating an operator whose expectation value depends only upon the 2-RDM [15, 31]. The T2 condition is more important than the T1 condition because it represents the probability distribution for a mixture of particles and holes. While the T2 condition can be readily added to the DQG conditions in the variational 2-RDM calculation in Eqs. (5-9), it has a much higher computational cost. Derived by Erdahl [13], the T2 condition was first implemented by Braams and co-workers [30] at a scaling of r^{12} in floating-point operations; shortly afterwards, it was implemented by the author by first-order semidefinite programming [31, 32] at a scaling of r^9 in floating-point operations and r^6 in storage.

Variational 2-RDM theory can also be expressed in a dual (polar) formulation in which the optimization is performed with respect to parameters in the N -representability conditions. In a finite basis set of r spin orbitals the ground-state energy E is computable by solving the following dual program

$$\max E \text{ such that } \hat{H} - E \hat{I} - \sum_i {}^2\hat{O}_i = 0 \quad (14)$$

where

$$\hat{H} = \sum_{ijkl} {}^2K_{kl}^{ij} \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_l \hat{a}_k \quad (15)$$

$${}^2\hat{I} = \sum_{ijkl} \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_l \hat{a}_k \quad (16)$$

and

$$\int {}^2\hat{O}_i {}^2D(12; \bar{1}\bar{2}) d1d2 \geq 0 \quad \forall {}^2D(12; \bar{1}\bar{2}) \in P_N^2. \quad (17)$$

The P_N^2 denotes the set of N -representable 2-RDMs. As the set of necessary N -representability conditions defined by the ${}^2\hat{O}_i$ operators is enlarged, the dual program converges to an increasingly better lower bound on the ground-state energy of the Hamiltonian \hat{H} in the finite basis set. By Kummer's bipolar theorem [12], for an equivalent set of N -representability conditions the energy from the solution of the dual program in Eqs. (14-17) equals the energy from the primal solution in Eqs. (5-9). In the limit that a complete set of N -representability conditions is included the energy from the dual program converges to the exact ground-state energy of \hat{H} .

In the dual formulation, the 2-positivity (DQG) conditions can be imposed by the following set of three linear operators:

$${}^2\hat{O}_D = \sum_{ijkl} {}^2B_D^{ij:kl} \hat{a}_i^\dagger \hat{a}_j^\dagger \hat{a}_l \hat{a}_k \quad (18)$$

$${}^2\hat{O}_Q = \sum_{ijkl} {}^2B_Q^{ij:kl} \hat{a}_i \hat{a}_j \hat{a}_l^\dagger \hat{a}_k^\dagger \quad (19)$$

$${}^2\hat{O}_G = \sum_{ijkl} {}^2B_G^{ij:kl} \hat{a}_i^\dagger \hat{a}_j \hat{a}_l^\dagger \hat{a}_k \quad (20)$$

where

$${}^2B_D \succeq 0 \quad (21)$$

$${}^2B_Q \succeq 0 \quad (22)$$

$${}^2B_G \succeq 0. \quad (23)$$

In the dual formulation the matrix elements of the operators ${}^2\hat{O}$ are the variational parameters instead of the 2-RDM elements. For $N = 2$ only the operators ${}^2\hat{O}_D$ are required to represent $(\hat{H} - E)$ with the ground-state energy E , but for $N > 2$ additional operators such as ${}^2\hat{O}_Q$ are required. Cancès, Stoltz, and Lewin previously implemented a related dual formulation of the DQG conditions [40]. Similarly, the T2 condition can be added by the following linear operator

$${}^2\hat{O}_{T2} = \sum_{ijkpqs} {}^3B_{T2}^{ijk;pqs} \left({}^3\hat{E}_{pqs}^{ijk} + {}^3\hat{F}_{pqs}^{ijk} \right) \quad (24)$$

where

$${}^3B_{T2} \succeq 0. \quad (25)$$

As discussed previously, the three-body operators in the sum of the ${}^3\hat{E}$ and ${}^3\hat{F}$ operators cancel, producing a two-body operator. As written, the dual formulation of the DQG and T2 conditions substituted into Eqs. (14-17) yields a semidefinite program [19, 21]. Without further modification first-order semidefinite programming can solve the dual program of the DQG conditions or the dual program of the DQG and T2 conditions at computational scalings similar to the solutions of the primal programs in Eqs. (5-13).

The computational scaling of the T2 condition in the dual formulation can be reduced by considering the structure of the Hamiltonian in Eq. (15). For quantum systems of electrons both the energy and the interaction term of the Hamiltonian scale linearly with system size. Consequently, the number of operators in Eq. (14) that describe the interaction must also scale linearly with system size. Linear scaling of the G and T2 constraints with system size can be restored by reducing the ranks of the 2B_G and ${}^3B_{T2}$ matrices to scale linearly with r , known in convex optimization as *rank reduction* [41, 42]. If at the solution the positive semidefinite matrices 2B_G and ${}^3B_{T2}$ have a low rank, then rank reduction does not affect the final solution of the semidefinite program. The rank reduction is imposed through a low-rank matrix factorization [19, 43–45]

$${}^2B_G^{ij;pq} = \sum_m^r C_m^{ij} C_{pq}^m \quad (26)$$

TABLE I. Correlation energies for a series of hydrogen chains at 1.5 Å are presented from variational 2-RDM calculations with DQG, DQGT, and rDQGT (rank reduced) constraints as well as FCI. FCI calculations are not possible for H₂₀ or H₃₀, requiring 24 billion and 36 quadrillion (10¹⁷) variables, but both DQG and rDQGT are applicable, requiring 800,000 and 4 million variables, respectively. The rDQGT energies are within 0.00001 a.u. of the DQGT energies.

Molecule	Energy (a.u.)	Correlation Energy (a.u.)			
	Hartree-Fock	DQG	DQGT	rDQGT	FCI
H ₄	-1.844789	-0.17283	-0.16789	-0.16789	-0.16789
H ₆	-2.773389	-0.26061	-0.24789	-0.24789	-0.24681
H ₈	-3.702789	-0.34998	-0.32867	-0.32867	-0.32536
H ₁₀	-4.632486	-0.43991	-0.40984	-0.40985	-0.40381
H ₂₀	-9.281963	-0.89174	–	-0.81817	–
H ₃₀	-13.931658	-1.34454	–	-1.22793	–

Rank reduction on 2B_G decreases the computational cost of the G condition in the dual formulation to r^5 floating-point operations and r^3 storage. Furthermore, rank reduction of ${}^3B_{T2}$ can be used to reduce the cost of the T2 condition to r^6 floating-point operations and r^4 storage, which is similar to the scaling of the DQG conditions in the primal program. A similar rank reduction can be performed for the T1 condition.

To illustrate, we apply the dual formulation variational 2-RDM theory to a series of hydrogen chains as well as a cadmium-selenide monomer and dimer. The ground-state energy is computed subject to the DQG and DQG plus T2 (DQGT) conditions by solving the dual program in Eqs. (14-17). Furthermore, we implement a rank-reduced version of the DQGT conditions, denoted rDQGT, in which the G and T2 conditions are rank reduced by low-ranked factorization. The DQG, DQGT, and rDQGT calculations use both spin and spatial symmetries [31]. The cadmium-selenide monomer and dimer are treated by [6,12] and [12,24] complete active-space calculations with respect to the Hartree-Fock orbitals. The notation [X,Y] indicates that X electrons in Y orbitals are correlated beyond mean field. Energies are compared with those from full configuration interaction (FCI) in the case of a hydrogen chains and with complete-active-space configuration interaction (CASCI) [46] in the case of the cadmium-selenide monomer.

Hydrogen chains exhibit a strongly correlated metal-to-insulator transition as the hydrogen atoms are separated equally [47]. Table I presents the correlation energies for a series of hydrogen chains at 1.5 Å computed by DQG, DQGT, and rDQGT and compared with FCI. The correlation energy at 1.5 Å is difficult to describe because the chain is in the middle of the metal-to-insulator transition after the onset of strong electron correlation. At 1.5 Å single-reference methods such as coupled cluster singles-doubles and parametric 2-RDM methods either fail to converge or yield unphysical results [19–21].

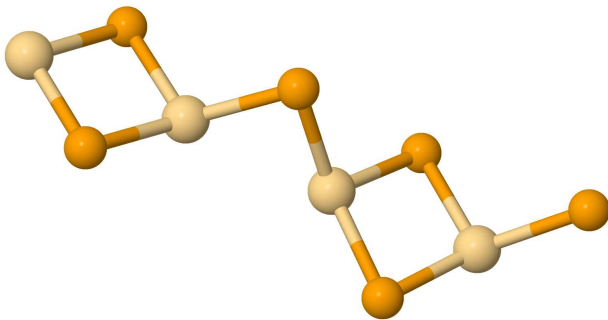


FIG. 1. The crystallographic structure of the $(\text{Cd}_2\text{Se}_3^{-2})_2$ dimer is displayed.

TABLE II. The numbers of variables in the 2-RDM and FCI calculations are shown. Rank reduction in the dual formulation (rDQGT) reduces the number of variables from DQGT by two orders of magnitude for the monomer and two-and-a-half orders of magnitude for the dimer. Furthermore, the rDQGT calculations require slightly fewer variables than the DQG calculations for both the monomer and the dimer.

Molecule	DQG	Number of Variables		FCI
		DQGT	rDQGT	
$\text{Cd}_2\text{Se}_3^{-2}$	1.8×10^5	1.4×10^7	1.5×10^5	8.5×10^5
$\text{Cd}_4\text{Se}_6^{-4}$	3.0×10^6	9.3×10^8	2.4×10^6	7.3×10^{12}

TABLE III. The correlation energies from the 2-RDM and FCI calculations are shown. As in hydrogen chains, the rDQGT energies significantly improve upon the DQG energies despite their similar computational costs. For the monomer the rDQGT energy is only 0.00002 a.u. below the DQGT energy.

Molecule	Energy (a.u.) Hartree-Fock	Correlation Energy (a.u.)			
		DQG	DQGT	rDQGT	FCI
$\text{Cd}_2\text{Se}_3^{-2}$	-17825.37999	-0.14235	-0.13152	-0.13154	-0.12733
$\text{Cd}_4\text{Se}_6^{-4}$	-35650.55450	-0.56188	—	-0.50863	—

The most important result in Table I is that the energies from rDQGT are within 0.00001 a.u. of the energies from DQGT. The rDQGT and DQGT energies are in equally good agreement at other bond lengths. Second, the rDQGT energies significantly improve upon those from DQG with minimal differences in both memory storage and floating-point operations. For example, for H_4 the energy from DQG is -0.005 a.u. below FCI while the energies from DQGT and rDQGT are exact; for H_{30} the rDQGT energy is above the DQG energy by more than 0.116 a.u. Both rDQGT and DQG have similar numbers of variables, and the relative timings of the rDQGT calculations range from 2 times faster to 2-to-3 times slower than the DQG calculations. Finally, while FCI calculations are not possible for H_{20} or H_{30}

where they would require computing with 24 billion and 36 quadrillion (10^{17}) variables, respectively, both DQG and rDQGT are applicable, requiring in the case of H_{20} less than 800,000 variables and in the case of H_{30} less than 4 million variables.

Talpin and coworkers [48, 49] have recently shown that the photovoltaic efficiency of nanocrystalline arrays can be significantly improved with the addition of $\text{Na}_2\text{Cd}_2\text{Se}_3$. X-ray crystallography reveals that the $\text{Cd}_2\text{Se}_3^{-2}$ anions polymerize to form dimers and longer polymers that act as electronic “glue” between nanoparticles, enhancing conductivity through the array. Figure 1 shows the crystallographic structure of the dimer [49]. Eigenvalues of the 1-RDM, known as natural occupation numbers, from 2-RDM calculations with DQG conditions reveal that the monomer and the dimer are strongly correlated. The observation of strong correlation is consistent with their experimental role as conductors [48, 49]. Here we present dual calculations of the correlation energies with the DQG, DQGT, and rDQGT conditions where the monomer and dimer are treated in [6,12] and [12,24] active spaces.

The number of variables required by the calculations, presented in Table II, shows that rDQGT reduces the number of variables from DQGT by two orders of magnitude for the monomer and two-and-a-half orders of magnitude for the dimer. Furthermore, the rDQGT calculations require slightly fewer variables than the DQG calculations for both the monomer and the dimer. While rDQGT and CASCI have relatively similar numbers of variables for the monomer, CASCI of the dimer, if possible, would require 7 trillion variables. Correlation energies are shown in Table III. For the monomer the rDQGT energy is only 0.00002 a.u. below the DQGT energy. As in hydrogen chains, the rDQGT energies significantly improve upon the DQG energies. Although the presented calculations are performed in a minimal basis set without counter ions, we observe that, while the Hartree-Fock energies do not predict binding, the addition of the electron correlation energy is sufficient to stabilize the dimer relative to two monomers.

Strongly correlated quantum systems from molecules to spin systems like the Hubbard and Erdahl models have been accurately treated by the variational 2-RDM calculations with the T2 N -representability condition. However, the computational cost of the T2 condition has limited its application to treat strong electron correlation in larger systems. In this Letter a dramatic reduction in the computational scaling of the T2 condition has been presented through a low-rank dual formulation where the rank reduction is based on the locality of the Hamiltonian interaction. We observe in computations on both hydrogen chains and a cadmium selenide dimer that the rank reduction does not affect the accuracy of the computed energies. The maximum error for the rank reduction was 2×10^{-5} a.u. Future extensions of the present

work will (i) improve the efficiency of the implementation (the current version was largely written in the interpretive language rather than a compiled language) and (ii) compute the 2-RDM from the dual solution. The present work also provides an efficient dual framework for the addition of constraints beyond T2 from the hierarchy of N -representability conditions of Ref. 15. The dual description has had an important role in 2-RDM theory in the development of both N -representability conditions [1, 2, 11–13, 15, 34] and semidefinite programming algorithms [16, 19, 21, 30, 40, 50]. Here the dual description in combination with rank reduction has been applied to enhancing the efficiency of the T2 condition. The low-scaling T2 condition in variational 2-RDM theory will become a standard tool for the accurate treatment of strong electron correlation with applications to molecular quantum systems throughout physics and chemistry.

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