REPORT DOCUMENTATION PAGE

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15-05-2020	Final Report	15-Apr-2016 - 14-Apr-2020

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Final Report: Effect of Strong Electron Correlation in the Description and Design of Efficient Energy-Transfer Mechanisms

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5b. GRANT NUMBER

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University of Chicago
5801 South Ellis Avenue

Chicago, IL 60637 -5418

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Approved for public release; distribution is unlimited.

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The views, opinions and/or findings contained in this report are those of the author(s) and should not contrued as an official Department of the Army position, policy or decision, unless so designated by other documentation.

14. ABSTRACT

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	15. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			David Mazziotti
UU	UU	UU	UU		19b. TELEPHONE NUMBER 773-834-1762

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as of 07-Jul-2020

Agency Code:

Proposal Number: 65574CH **Agreement Number: W911NF-16-1-0152**
INVESTIGATOR(S):

Name: David Mazziotti
Email: damazz@uchicago.edu
Phone Number: 7738341762
Principal: Y

Organization: **University of Chicago**
Address: 5801 South Ellis Avenue, Chicago, IL 606375418
Country: USA
DUNS Number: 005421136 EIN: 362177139
Report Date: 14-Jul-2020 Date Received: 15-May-2020
Final Report for Period Beginning 15-Apr-2016 and Ending 14-Apr-2020
Title: Effect of Strong Electron Correlation in the Description and Design of Efficient Energy-Transfer Mechanisms
Begin Performance Period: 15-Apr-2016 **End Performance Period:** 14-Apr-2020
Report Term: 0-Other
Submitted By: David Mazziotti Email: damazz@uchicago.edu
Phone: (773) 834-1762
Distribution Statement: 1-Approved for public release; distribution is unlimited.

STEM Degrees: 2 **STEM Participants:** 2

Major Goals: The major goal of the project is the description and prediction of energy-transfer mechanisms in the presence of strong electron correlation. Present methodologies are limited in their ability to treat strong electron correlation in energy-transfer processes. The scientific opportunity is that: traditional descriptions of strongly correlated molecules scale exponentially with the number of electrons, but recent research in my lab and elsewhere has opened new opportunities for treating strong correlation with polynomial cost through the direct calculation of the two-electron reduced density matrix (2-RDM). Under the grant we are working to: (1) develop 2-RDM-based theories for (a) predicting electron transfer in strongly correlated molecules, (b) predicting molecular conductivity in strongly correlated molecules, and (c) predicting exciton condensation in molecular systems. The impact lies in the fact that the treatment of strong electron correlation at polynomial cost transforms our ability to predict strongly correlated molecules and materials. Research will enable the design of highly efficient energy-transfer mechanisms relevant to ARMY/DOD mission.

Accomplishments: See PDF Document

Training Opportunities: Significant research has been accomplished uner the Army Research Office (Grant No. W911NF-16-1-0152). The research produced 40 published papers and partially supported the training of 2 postdoctoral students, 16 graduate students, and 5 undergraduate students. Students performed research and reported results in
publications and presentations at international meetings including the American Chemical Society National Meetings 2019 and the Sanibel Symposium 2019.

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Results Dissemination: The research produced 40 published papers overall. Results were presented at invited lectures and international workshops and conferences. Three press releases were issued:

https://news.uchicago.edu/story/less-more-when-it-comes-predicting-molecules-conductivity

https://news.uchicago.edu/story/scientists-tap-open-access-quantum-computer-tease-out-quantum-secrets

and

https://news.uchicago.edu/story/uchicago-scientists-predict-new-state-matter

Research was also the topic of a special news article in Physics World in 2020

https://physicsworld.com/a/dual-condensate-of-fermions-and-excitons-should-exist-say-theoretical-chemists/

Honors and Awards: The PI was recognized as the Mulliken Invited Lecturer at the University of Georgia, Athens in 2018.

Protocol Activity Status:

Technology Transfer: The graduate student A. W. Schlimgen graduated and started a position as LANL. Research codes for 2-RDM computations were released in conjunction with RDMChem and Maplesoft in the new commercial package, Maple Quantum Chemistry Package.

PARTICIPANTS:

Participant Type: Graduate Student (research assistant)
Participant: LeeAnn Sager
Person Months Worked: 4.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: Jan-Niklas Boyn
Person Months Worked: 8.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: Scott Smart
Person Months Worked: 6.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)

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Participant: Shiva Safaei
Person Months Worked: 9.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: Simon Ewing
Person Months Worked: 6.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Graduate Student (research assistant)
Participant: Kade Head-Marsden
Person Months Worked: 4.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)
Participant: Shayan Hemmatiyan
Person Months Worked: 6.00 **Funding Support:**
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

ARTICLES:

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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: The Journal of Chemical Physics
Publication Identifier Type: DOI Publication Identifier: 10.1063/1.4959872
Volume: 145 Issue: 6 First Page #: 064101
Date Submitted: 8/30/16 12:00AM Date Published: 8/1/16 5:00AM
Publication Location:
Article Title: Accurate non-adiabatic quantum dynamics from pseudospectral sampling of time-dependent Gaussian basis sets
Authors: Charles W. Heaps, David A. Mazziotti
Keywords: nonadiabatic dynamics, electronic structure, pseudospectral methods
Abstract: Quantum molecular dynamics requires an accurate representation of the molecular potential energy surface from a minimal number of electronic structure calculations, particularly for nonadiabatic dynamics where excited states are required. In this paper, we employ pseudospectral sampling of time-dependent Gaussian basis functions for the simulation of non-adiabatic dynamics. Unlike other methods, the pseudospectral Gaussian molecular dynamics tests the Schrödinger equation with N Dirac delta functions located at the centers of the Gaussian functions reducing the scaling of potential energy evaluations from O(N2) to O(N). By projecting the Gaussian basis onto discrete points in space, the method is capable of efficiently and quantitatively describing the nonadiabatic population transfer and intra-surface quantum coherence. We investigate three model systems: the photodissociation of three coupled Morse oscillators, the bound state dynamics of two coupled Morse oscillators, and a two-dime
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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Phys. Chem. Chem. Phys.
Publication Identifier Type: DOI Publication Identifier: 10.1039/C6CP07563K
Volume: 19 Issue: 6 First Page #: 4656
Date Submitted: 2/20/17 12:00AM Date Published:
Publication Location:
Article Title: Ligand non-innocence and strong correlation in manganese superoxide dismutase mimics
Authors: Alexandra R. McIsaac, David A. Mazziotti
Keywords: superoxide dismutase mimics, large active spaces, variational two-electron reduced density matrix method
Abstract: We examine the 1-electron reduction of manganese porphyrin complexes Mn(III) porphyrin and Mn(III) TDE-2-ImP5+, which have attracted recent interest due to their properties as superoxide dismutase mimics. We perform a series of electronic structure calculations using the variational 2-electron reduced density matrix (2-RDM) method with a large [30,30] active space that represents a wavefunction with 1019 variables, as well as the more traditional complete active space self-consistent field (CASSCF) method with a [14,14] active space. We show that the larger 2-RDM calculation, intractable with CASSCF, is required to capture the full effects of electron correlation in the molecule and predict the non-innocence of the porphyrin ligand during the reduction. The CASSCF method predicts single-reference systems exhibiting a metal-centered reduction, but the 2-RDM method predicts a strongly correlated system exhibiting a ligand-centered reduction.
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Journal: Physical Review Letters
Publication Identifier Type: DOI Publication Identifier: 10.1103/PhysRevLett.117.153001
Volume: 117 Issue: 15 First Page #:
Date Submitted: 2/20/17 12:00AM Date Published: 10/1/16 5:00AM
Publication Location:
Article Title: Enhanced Constraints for Accurate Lower Bounds on Many-Electron Quantum Energies from Variational Two-Electron Reduced Density Matrix Theory
Authors: David A. Mazziotti
Keywords: lower bounds, reduced density matrices
Abstract: A central challenge of physics is the computation of strongly correlated quantum systems. The past ten 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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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Physical Review A
Publication Identifier Type: DOI Publication Identifier: 10.1103/PhysRevA.94.032516
Volume: 94 Issue: 3 First Page #:
Date Submitted: 2/20/17 12:00AM Date Published: 9/1/16 5:00AM
Publication Location:
Article Title: Pure-N-representability conditions of two-fermion reduced density matrices
Authors: David A. Mazziotti
Keywords: electron correlation, generalized Pauli constraints
Abstract: We derive necessary conditions for any two-fermion reduced density matrix (2-RDM) to be representable by a pure N-fermion density matrix ??? where ? is the wave function. These pure N-representability conditions of the 2-RDM are important because they provide stringent constraints beyond those from the Pauli and the generalized Pauli constraints on the structure of many-fermion 2-RDMs and their wave functions. The pure 2-RDM conditions are derived as generalized Pauli constraints on effective one-fermion reduced density matrices (1-RDMs) generated by the removal or addition of a fermion from the wave function. Computationally, we show for four-electron molecules that the derived pure N-representability conditions are nontrivially active for exact ground-state 2-RDMs and that they provide significant restrictions beyond the D, Q, and G ensemble N-representability conditions. Constraints on higher-order p-RDMs where p>2 are derived in a similar fashion.
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Publication Identifier Type: DOI Publication Identifier: 10.1002/qua.25120
Volume: 116 Issue: 10 First Page #: 784
Date Submitted: 2/20/17 12:00AM Date Published: 5/1/16 10:00AM
Publication Location:
Article Title: Role of the generalized pauli constraints in the quantum chemistry of excited states
Authors: Romit Chakraborty, David A. Mazziotti
Keywords: generalized pauli constraints, excited states
Abstract: The Pauli exclusion principle requires that spin orbitals have occupations between zero and one. For pure quantum systems, however, the occupations of the spin orbitals are constrained by additional inequalities known as the generalized Pauli constraints. If the occupation numbers saturate (or nearly saturate) the generalized Pauli constraints, then the occupation numbers are said to be pinned (or quasi-pinned) to the constraints. Here, we assess the complexity of electron correlation of excited states from the pinning or quasi-pinning of the occupation numbers to the generalized Pauli constraints where the degree of pinning encodes information about the structure of the wave function including correlation and entanglement. Results are presented for three- and four-electron atoms and molecules, the five-electron cyclopentadienyl radical, and the seven-electron Fenna-Matthews-Olson complex in green-sulfur bacteria.
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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: The Journal of Physical Chemistry A
Publication Identifier Type: DOI Publication Identifier: 10.1021/acs.jpca.7b00858
Volume: 121 Issue: 16 First Page #: 3142
Date Submitted: 8/30/17 12:00AM Date Published: 4/1/17 5:00AM
Publication Location:
Article Title: Orbitals, Occupation Numbers, and Band Structure of Short One-Dimensional Cadmium Telluride Polymers
Authors: Andrew J. S. Valentine, Dmitri V. Talapin, David A. Mazziotti
Keywords: inorganic ligands, 2-RDM calculations
Abstract: Recent work found that soldering CdTe quantum dots together with a molecular CdTe polymer yielded field-effect transistors with much greater electron mobility than quantum dots alone. We present a computational study of the CdTe polymer using the active-space variational two-electron reduced density matrix (2-RDM) method. While analogous complete active-space self-consistent field (CASSCF) methods scale exponentially with the number of active orbitals, the active-space variational 2-RDM method exhibits polynomial scaling. A CASSCF calculation using the (48o,64e) active space studied in this paper requires 1024 determinants and is therefore intractable, while the variational 2-RDM method in the same active space requires only 2.1 × 107 variables. Natural orbitals, natural-orbital occupations, charge gaps, and Mulliken charges are reported as a function of polymer length. The polymer, we find, is strongly correlated, despite possessing a simple sp3-hybridized bonding scheme.
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Journal: Chemical Physics Letters
Publication Identifier Type: DOI Publication Identifier: 10.1016/j.cplett.2017.07.064
Volume: 685 Issue: First Page #: 300
Date Submitted: 8/30/17 12:00AM Date Published: 10/1/17 5:00AM
Publication Location:
Article Title: Analytical nuclear derivatives for the parametric two-electron reduced density matrix method
Authors: Andrew J.S. Valentine, David A. Mazziotti
Keywords: analytical gradients
Abstract: Efficient and accurate nuclear gradients are essential to performing molecular optimizations. Here for the first time we present analytical nuclear gradients for the parametric two-electron reduced-density-matrix method (p2-RDM), which uses the 2-RDM as the primary variable in calculations in lieu of the many-electron wavefunction. While numerical gradients require six energy evaluations for each atom, analytical gradients require only a single calculation for each geometry sampled. We present benchmark p2-RDM geometry optimizations that show analytical gradients reduce CPU times by as much as 80%, even for small molecules. We also use p2-RDM to evaluate the bond length alternation (BLA), or the difference in length between adjacent single and double bonds, of trans-polyacetylene (PA). We find that the BLA in the extrapolated limit to be 0.080Å, in agreement with experiment and closely mirroring the prediction of the more expensive coupled-cluster with triple excitations.
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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: The Journal of Chemical Physics
Publication Identifier Type: DOI Publication Identifier: 10.1063/1.4982927
Volume: 146 Issue: 18 First Page #: 184101
Date Submitted: 8/30/17 12:00AM Date Published: 5/1/17 5:00AM
Publication Location:
Article Title: Noise-assisted energy transfer from the dilation of the set of one-electron reduced density matrices
Authors: Romit Chakraborty, David A. Mazziotti
Keywords: noise-assisted transport, generalized Pauli constraints
Abstract: Noise-assisted energy transfer can be explained geometrically in terms of the set of one-electron reduced density matrices (1-RDMs) [R. Chakraborty and D. A. Mazziotti, Phys. Rev. A 91, 010101(R) (2015)]. In this paper, we examine the geometric picture of quantum noise for the seven-chromophore Fenna-Matthews-Olson (FMO) complex. Noise expands the feasible set of orbital occupation trajectories to the target state through the violation of the pure-state N-representability conditions on the 1-RDM, known as the generalized Pauli constraints. While the generalized Pauli constraints are not explicitly known for seven-electron systems, we are able to treat a seven-exciton model of the FMO complex through the use of generalized Pauli constraints for p qubits which are known for arbitrary p.
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Volume: 147 Issue: 8 First Page #: 084101
Date Submitted: 8/30/17 12:00AM Date Published: 8/1/17 5:00AM
Publication Location:
Article Title: Pair 2-electron reduced density matrix theory using localized orbitals
Authors: Kade Head-Marsden, David A. Mazziotti
Keywords: pair theory
Abstract: Full configuration interaction (FCI) restricted to a pairing space yields size-extensive correlation energies but its cost scales exponentially with molecular size. Restricting the variational two-electron reduced-density-matrix (2-RDM) method to represent the same pairing space yields an accurate lower bound to the pair FCI energy at a mean-field-like computational scaling of O(r3) where r is the number of orbitals. In this paper, we show that localized molecular orbitals can be employed to generate an efficient, approximately size-extensive pair 2-RDM method. The use of localized orbitals eliminates the substantial cost of optimizing iteratively the orbitals defining the pairing space without compromising accuracy. In contrast to the localized orbitals, the use of canonical Hartree-Fock molecular orbitals is shown to be both inaccurate and non-size-extensive.
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Journal: Physical Review B
Publication Identifier Type: DOI Publication Identifier: 10.1103/PhysRevB.98.045122
Volume: 98 Issue: 4 First Page #:
Date Submitted: 7/28/18 12:00AM Date Published: 7/1/18 5:00AM
Publication Location:
Article Title: Quantum signature of exciton condensation
Authors: Shiva Safaei, David A. Mazziotti
Keywords: exciton condensation
Abstract: Exciton condensation, a Bose-Einstein-like condensation of excitons, was recently reported in an electronic double layer (EDL) of graphene. We show that a universal quantum signature for exciton condensation can be used to both identity and quantify exciton condensation in molecular systems from direct calculations of the two-electron reduced density matrix. Computed large eigenvalues in the particle-hole reduced-density matrices of pentacene and hexacene EDLs reveal the beginnings of condensation, suggesting the potential for exciton condensation in smaller scale molecular EDLs.
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Journal: The Journal of Chemical Physics
Publication Identifier Type: DOI Publication Identifier: 10.1063/1.5024512
Volume: 149 Issue: 2 First Page #: 024302
Date Submitted: 7/28/18 12:00AM Date Published: 7/1/18 5:00AM
Publication Location:
Article Title: Using reduced density matrix techniques to capture static and dynamic correlation in the energy landscape for the decomposition of the CH
Authors: Scott E. Smart, Preston G. Scrape, Laurie J. Butler, David A. Mazziotti
Keywords: alkyl nitrates
Abstract: The unexpected abundance of HNO in the photodecomposition of the radical 2-nitrosooxy ethyl (CH2CH2ONO) is investigated through calculations of the potential energy surface by the anti-Hermitian contracted Schrödinger equation (ACSE) method, which directly generates the 2-electron reduced density matrix. The ACSE, which is able to balance single-reference (dynamic) and multi-reference (static) correlation effects, reveals some subtle correlation effects along the intrinsic reaction coordinate (IRC) en route to NO + oxirane, an IRC which offers a potential bifurcation to the HNO + vinoxy product channel. These effects were not fully captured by either single-reference techniques, such as coupled cluster, or multi-reference techniques, such as second-order multi-reference perturbation theory. These correlation effects reveal small to moderate energy changes in key transition states, which have implications for the reaction mechanism as related to the production of HNO.
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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Physical Review A
Publication Identifier Type: DOI Publication Identifier: 10.1103/PhysRevA.97.062502
Volume: 97 Issue: 6 First Page #:
Date Submitted: 7/28/18 12:00AM Date Published: 6/1/18 12:00AM
Publication Location:
Article Title: Entangling and disentangling many-electron quantum systems with an electric field
Authors: Manas Sajjan, Kade Head-Marsden, David A. Mazziotti
Keywords: electric field, entanglement
Abstract: We show that the electron correlation of a molecular system can be enhanced or diminished through the application of a homogeneous electric field antiparallel or parallel to the system's intrinsic dipole moment. More generally, we prove that any external stimulus that significantly changes the expectation value of a one-electron operator with nondegenerate minimum and maximum eigenvalues can be used to control the degree of a molecule's electron correlation. Computationally, the effect is demonstrated in HeH+, MgH+, BH, HCN, H2O, HF, formaldehyde, and a fluorescent dye. Furthermore, we show in calculations with an array of formaldehyde (CH2O) molecules that the field can control not only the electron correlation of a single formaldehyde molecule but also the entanglement among formaldehyde molecules. The quantum control of correlation and entanglement has potential applications in the design of molecules with tunable properties and the stabilization of qubits in quantum computations.
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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Communications Chemistry
Publication Identifier Type: DOI Publication Identifier: 10.1038/s42004-018-0030-2
Volume: 1 Issue: 1 First Page #:
Date Submitted: 7/28/18 12:00AM Date Published: 5/1/18 5:00AM
Publication Location:
Article Title: Current-constrained density-matrix theory to calculate molecular conductivity with increased accuracy
Authors: Manas Sajjan, David A. Mazziotti
Keywords: molecular conduction
Abstract: Molecular conductivity is the quantum flow of electrons through a molecule. Since its conception by Aviram and Ratner, molecular conductivity has been realized experimentally in molecules and molecular-scale circuits. Significant challenges, however, remain for its prediction with popular theoretical methods often overpredicting conductance by as much as an order of magnitude. Here we report a current-constrained, electronic structure-based variational principle for molecular conductivity. Unlike existing theories, which set the voltage to compute the current, the current-constrained variational principle determines the voltage from an electronic structure calculation in which the current is added as a constraint. We apply the variational principle to benezenedithiol with gold and nickel leads where it matches experimental values and trends, improving upon previous theory by as much as 1–2 orders of magnitude. The current constraint produces a conducting steady state that includes all
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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: The Journal of Physical Chemistry A
Publication Identifier Type: DOI Publication Identifier: 10.1021/acs.jpca.8b00941
Volume: 122 Issue: 22 First Page #: 4988
Date Submitted: 7/28/18 12:00AM Date Published: 5/1/18 12:00AM
Publication Location:
Article Title: Strong Electron Correlation in Nitrogenase Cofactor, FeMoco
Authors: Jason M. Montgomery, David A. Mazziotti
Keywords: FeMoco
Abstract: FeMoco, MoFe7S9C, has been shown to be the active catalytic site for the reduction of nitrogen to ammonia in the nitrogenase protein. An understanding of its electronic structure including strong electron correlation is key to designing mimic catalysts capable of ambient nitrogen fixation. Active spaces ranging from [54, 54] to [65, 57] have been predicted for a quantitative description of FeMoco's electronic structure. However, a wave function approach for a singlet state using a [54, 54] active space would require 1029 variables. In this work, we systematically explore the active-space size necessary to qualitatively capture strong correlation in FeMoco and two related moieties, MoFe3S7 and Fe4S7. Using CASSCF and 2-RDM methods, we consider active-space sizes up to [14, 14] and [30, 30], respectively, with STO-3G, 3-21G, and DZP basis sets and use fractional natural-orbital occupation numbers to assess the level of multireference electron correlation, an examination of which reveals
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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: Molecular Physics
Publication Identifier Type: DOI Publication Identifier: 10.1080/00268976.2018.1430386
Volume: 116 Issue: 10 First Page #: 1364
Date Submitted: 7/28/18 12:00AM Date Published: 2/1/18 6:00AM
Publication Location:
Article Title: Effects of nitrogenous substituent groups on the benzene dication
Authors: C. C. Forgy, A. W. Schlimgen, D. A. Mazziotti
Keywords: reduced density matrices
Abstract: The benzene dication possesses a pentagonal-pyramidal structure with a hexacoordinated carbon. In contrast, halogenated benzene dications retain a similar structure to their parent molecules. In this work, we report on theoretical studies of the structures of the dications of benzene with nitrogenous substituents. We find that the nitrobenzene dication favours a near ideal pentagonal-pyramidal structure, while the aniline dication favours a flat, hexagonal structure. Reduced-density-matrices methods give predictions in agreement with available ab initio calculations and experiment. These results are also compared with those from the Hartree–Fock method and density functional theory.
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Publication Type: Journal Article Peer Reviewed: Y **Publication Status:** 1-Published
Journal: The Journal of Chemical Physics
Publication Identifier Type: DOI Publication Identifier: 10.1063/1.5010985
Volume: 148 Issue: 5 First Page #: 054106
Date Submitted: 7/28/18 12:00AM Date Published: 2/1/18 12:00AM
Publication Location:
Article Title: Sparsity of the wavefunction from the generalized Pauli exclusion principle
Authors: Romit Chakraborty, David A. Mazziotti
Keywords: generalized Pauli constraints
Abstract: Electron occupations that arise from pure quantum states are restricted by a stringent set of conditions that are said to generalize the Pauli exclusion principle. These generalized Pauli constraints (GPCs) define the boundary of the set of one-electron reduced density matrices (1-RDMs) that are derivable from at least one N-electron wavefunction. In this paper, we investigate the sparsity of the Slater-determinant representation of the wavefunction that is a necessary, albeit not sufficient, condition for its 1-RDM to lie on the boundary of the set of pure N-representable 1-RDMs or in other words saturate one of the GPCs. The sparse wavefunction, we show, is exact not only for 3 electrons in 6 orbitals but also for 3 electrons in 8 orbitals. For larger numbers of electrons and/or orbitals in the lowest spin state, the exact wavefunction does not generally saturate one of the GPCs, and hence, the sparse representation is typically an approximation.
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Article Title: Static and Dynamic Electron Correlation in the Ligand Noninnocent Oxidation of Nickel Dithiolates
Authors: Anthony W. Schlimgen, David A. Mazziotti
Keywords: strong correlation
Abstract: Metal dithiolates have a wide range of applications from catalysis to molecular conductors with the ligands being the source of electrons during electrochemical oxidation in an effect known as ligand noninnocence. Recent large-scale variational two-electron reduced-density matrix (2-RDM) calculations of the vanadium oxo complex and manganese superoxide dismutase show that quantum entanglement stabilizes the addition of an electron to the ligands, providing a quantum mechanical explanation for ligand noninnocence. In this paper, we confirm and explore the ligand noninnocence in the electron oxidation series of bis(ethylene-1,2-dithiolato)nickel or [Ni(edt2)](?2,–1,0) with variational 2-RDM calculations. While previous wave function calculations of this series have selected only the ligand ? orbitals as the critical (active) orbitals to be correlated, we find that both ligand ? and nickel d orbitals must be correlated to generate a realistic picture of the electron-transfer process. Usin
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Publication Identifier Type: DOI Publication Identifier: 10.1063/1.4986804
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Date Submitted: 7/28/18 12:00AM Date Published: 11/1/17 5:00AM
Publication Location:
Article Title: Development and application of a 2-electron reduced density matrix approach to electron transport via molecular junctions
Authors: Erik P. Hoy, David A. Mazziotti, Tamar Seideman
Keywords: transport, NEGF
Abstract: Can an electronic device be constructed using only a single molecule? Since this question was first asked by Aviram and Ratner in the 1970s [Chem. Phys. Lett. 29, 277 (1974)], the field of molecular electronics has exploded with significant experimental advancements in the understanding of the charge transport properties of single molecule devices. Efforts to explain the results of these experiments and identify promising new candidate molecules for molecular devices have led to the development of numerous new theoretical methods including the current standard theoretical approach for studying single molecule charge transport, i.e., the non-equilibrium Green’s function formalism (NEGF).
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Date Submitted: 10/7/19 12:00AM Date Published: 7/1/19 5:00AM
Publication Location:
Article Title: Satisfying fermionic statistics in the modeling of non-Markovian dynamics with one-electron reduced density matrices
Authors: Kade Head-Marsden, David A. Mazziotti
Keywords: fermions, non-Markov
Abstract: Treatment of Markovian, many-electron dynamics from the solution of the Lindblad equation for the 1-electron reduced density matrix requires additional constraints on the bath operators to maintain fermion statistics. Recently, we generalized Lindblad's formalism to non-Markovian dynamics through an ensemble of Lindbladian trajectories. Here we show that the fermion statistics of non-Markovian dynamics can be enforced through analogous constraints on the bath operators of each Lindbladian trajectory in the ensemble. To illustrate, we apply the non-Markovian method to three distinct systems of two fermions in three levels. While the electrons violate the fermion statistics without the constraints, correct fermion behavior is recovered with the constraints.
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Date Submitted: 10/7/19 12:00AM Date Published: 6/1/19 5:00AM
Publication Location:
Article Title: Unraveling the Band Gap Trend in the Narrowest Graphene Nanoribbons from the Spin-Adapted Excited-Spectra Reduced Density Matrix Method
Authors: Shayan Hemmatiyan, David A. Mazziotti
Keywords: excited-state spectra, graphene
Abstract: Polybenzenes as the narrowest graphene nanoribbons with versatile electronic properties are widely studied both theoretically and technologically. Here, we examine the singlet-triplet band gap as a function of length for two members of the oligobenzene family: the acene and phenacene chains. We observe that the prediction of the band gap is highly sensitive to the accurate treatment of the electron correlation. The excited-spectra two-electron reduced density matrix (2-RDM) method, which computes the excited states from a variationally computed ground-state 2-RDM, yields finite band gaps for all finite chain lengths through 10 rings as well as in the extrapolated infinite ring limits of both acenes and phenacenes. In contrast, we find that weakly correlated methods like configuration interaction singles and time-dependent density functional theory predict a crossing of the singlet- and triplet-state energies of the acene chains at a finite ring size, with the triplet becoming the energ
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Volume: 150 Issue: 14 First Page #: 144102
Date Submitted: 10/7/19 12:00AM Date Published: 4/1/19 5:00AM
Publication Location:
Article Title: Sparse non-orthogonal wave function expansions from the extension of the generalized Pauli constraints to the two-electron reduced density matrix
Authors: Jan-Niklas Boyn, David A. Mazziotti
Keywords: generalized Pauli constraints
Abstract: Generalized Pauli constraints (GPCs) impose constraints in the form of inequalities on the natural orbital occupation numbers of the one electron reduced density matrix (1-RDM), defining the set of pure N-representable 1-RDMs, or 1-RDMs that can be derived from an N-electron wave function. Saturation of these constraints is termed "pinning" and implies a significant simplification of the N-electron wave function as the number of Slater determinants required to fully describe the system is reduced. Recent research has shown pinning to occur for the ground states of atoms and molecules with N = 3 and r = 6, where N is the number of electrons and r is the number of spin orbitals. For N = 4 and r = 8, however, pinning occurs not to the GPCs but rather to inequalities defining the pure N-representable two-electron reduced density matrices (2-RDMs). Using these more general inequalities, we derive a wave function ansatz for a system with four electrons in eight spin orbitals.
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Volume: 99 Issue: 2 First Page #:
Date Submitted: 10/7/19 12:00AM Date Published: 2/1/19 6:00AM
Publication Location:
Article Title: Ensemble of Lindblad's trajectories for non-Markovian dynamics
Authors: Kade Head-Marsden, David A. Mazziotti
Keywords: Lindblad, non-Markov
Abstract: Although Lindblad developed a general Markovian theory for open-system dynamics while maintaining the positivity of the density matrix, a practical non-Markovian analog remains a significant problem. Here, we present an extension of Lindblad's theory through an ensemble of Lindbladian trajectories originating from different times in the system's history. This approach provides an account of the system's memory while preserving the positivity of the density matrix. We apply the theory to the Jaynes-Cummings model to capture non-Markovian dynamics in the weak and strong coupling regimes.
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Volume: 2 Issue: 1 First Page #:
Date Submitted: 10/7/19 12:00AM Date Published: 1/1/19 6:00AM
Publication Location:
Article Title: Experimental data from a quantum computer verifies the generalized Pauli exclusion principle
Authors: Scott E. Smart, David I. Schuster, David A. Mazziotti
Keywords: quantum computer, electronic structure
Abstract: "What are the consequences. that Fermi particles cannot get into the same state."R.P. Feynman wrote of the Pauli exclusion principle, "In fact, almost all the peculiarities of the material world hinge on this wonderful fact." In 1972 Borland and Dennis showed that there exist powerful constraints beyond the Pauli exclusion principle on the orbital occupations of Fermi particles, providing important restrictions on quantum correlation and entanglement. Here we use computations on quantum computers to experimentally verify the existence of these additional constraints. Quantum many-fermion states are randomly prepared on the quantum computer and tested for constraint violations. Measurements show no violation and confirm the generalized Pauli exclusion principle with an error of one part in one quintillion.
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Volume: 100 Issue: 2 First Page #:
Date Submitted: 10/7/19 12:00AM Date Published: 8/1/19 5:00AM
Publication Location:
Article Title: Quantum-classical hybrid algorithm using an error-mitigating
Authors: Scott E. Smart, David A. Mazziotti
Keywords: quantum computer, reduced density matrices
Abstract: Quantum algorithms for molecular electronic structure have been developed with lower computational scaling than their classical counterparts, but emerging quantum hardware is far from being capable of the coherence, connectivity, and gate errors required for their experimental realization. Here we propose a class of quantum-classical hybrid algorithms that computes the energy from a two-electron reduced density matrix (2-RDM). The 2-RDM is constrained by N-representability conditions, constraints for representing an N-electron wave function, which mitigate noise from the quantum circuit. We compute the strongly correlated dissociation of doublet H3 into three hydrogen atoms. The hybrid quantum-classical computer matches the energies from full configuration interaction to 0.1 kcal/mol, one-tenth of “chemical accuracy,” even in the strongly correlated limit of dissociation. Furthermore, the spatial locality of the computed one-electron RDM reveals that the quantum computer accurately pre
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Date Submitted: 10/7/19 12:00AM Date Published: 10/1/18 5:00AM
Publication Location:
Article Title: Analytical gradients of variational reduced-density-matrix and wavefunction-based methods from an overlap-reweighted semidefinite program
Authors: Anthony W. Schlimgen, David A. Mazziotti
Keywords: analytical gradients, reduced density matrix theory
Abstract: Analytical gradients of variational two-electron reduced-density matrix (2-RDM) methods are derived by transforming the atomic-orbital reduced-density matrices to remove the dependence of the N-representability conditions on the orbital-overlap matrix. The transformation, performed through a Cholesky decomposition of the geminal-overlap matrix, generates a Hellmann-Feynman-like expression for the gradient that only depends on the derivative of the transformed reduced Hamiltonian matrix. The formulation is applicable not only to the variational 2-RDM method but also to variational wavefunction methods like the full configuration interaction and complete active-space self-consistent-field. To illustrate, we apply the analytical gradients to perform geometry optimizations on several transition metal complexes, octahedral and trigonal prismatic CrF6 as well as the (ethylene-1,2-dithiolato)nickel, or Ni(edt)(2), complex. Published by AIP Publishing.
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Date Submitted: 10/7/19 12:00AM Date Published: 9/1/18 5:00AM
Publication Location:
Article Title: Excited-State Spectra of Strongly Correlated Molecules from a Reduced-Density-Matrix Approach
Authors: S. Hemmatiyan, M. Sajjan, A. W. Schlimgen, D. A. Mazziotti
Keywords: excited energy spectra
Abstract: Excited-state energies are computed in the space of single-electron transitions from the ground state from only a knowledge of the two-electron reduced density matrix (2-RDM). Previous work developed and applied the theory to small molecular systems with accurate results, but applications to both larger and more correlated molecules were hindered by ill-conditioning of the effective eigenvalue problem. Here we improve the excited-spectra 2-RDM theory through a stable Hamiltonian-shifted regularization algorithm that removes the near singularities within the computation. The theory with ground-state 2-RDMs from the variational 2-RDM method is applied to the excited energies of strongly correlated molecules including the optical band gap of hydrogen and acene chains, the singlet-triplet splitting of nickel dithiolates, as well as the low-lying excited states of an optical dye. While single-excitation theories like CISD and TD-DFT underestimate band gaps and excited-state splittings, the
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Volume: 21 Issue: 23 First Page #: 12620
Date Submitted: 10/7/19 12:00AM Date Published: 5/21/19 5:00AM
Publication Location:
Article Title: Current-constrained one-electron reduced density-matrix theory for non-equilibrium steady-state molecular conductivity
Authors: Alexandra E. Raeber, David A. Mazziotti
Keywords: molecular conductivity
Abstract: In the effort to create ever smaller electronic devices, the idea of single molecule circuit elements has sparked the imagination of scientists for nearly fifty years. While traditional theories for non-equilibrium steady-state molecular conductivity like the non-equilibrium Green's function density functional theory determine the current from an applied voltage, the recently proposed current-constrained density-matrix theory computes the voltage from a current constraint on the molecule. In the present paper we extend the current-constrained density-matrix theory from its two-electron reduced density-matrix (2-RDM) formulation to a one-electron reduced density matrix (1-RDM) formulation that is applicable to Hartree–Fock, density functional, and tight-binding theories. We demonstrate the current-constrained 1-RDM method through the computation of the theoretical, intrinsic resistance of acenes and phenacenes.
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Volume: 11 Issue: 4 First Page #: 1066
Date Submitted: 5/15/20 12:00AM Date Published: 1/10/20 6:00AM
Publication Location:
Article Title: Redox, transmetalation, and stacking properties of tetrathiafulvalene-2,3,6,7-tetrathiolate bridged tin, nickel, and palladium compounds
Authors: Jiaze Xie, Jan-Niklas Boyn, Alexander S. Filatov, Andrew J. McNeece, David A. Mazziotti, John S. Ande
Keywords: variational 2-RDM theory
Abstract: Here we report that capping the molecule TTFtt (TTFtt = tetrathiafulvalene-2,3,6,7-tetrathiolate) with dialkyl tin groups enables the isolation of a stable series of redox congeners and facile transmetalation to Ni and Pd. TTFtt has been proposed as an attractive building block for molecular materials for two decades as it combines the redox chemistry of TTF and dithiolene units. TTFttH4, however, is inherently unstable and the incorporation of TTFtt units into complexes or materials typically proceeds through the in situ generation of the tetraanion TTFtt4?. Capping of TTFtt4? with Bu2Sn2+ units dramatically improves the stability of the TTFtt moiety and furthermore enables the isolation of a redox series where the TTF core carries the formal charges of 0, +1, and +2. All of these redox congeners show efficient and clean transmetalation to Ni and Pd resulting in an analogous series of bimetallic complexes capped by 1,2-bis(diphenylphosphino)ethane (dppe) ligands.
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Volume: 101 Issue: 8 First Page #:
Date Submitted: 5/15/20 12:00AM Date Published: 2/1/20 6:00AM
Publication Location:
Article Title: Potential coexistence of exciton and fermion-pair condensations
Authors: LeeAnn M. Sager, Shiva Safaei, David A. Mazziotti
Keywords: exciton condenates, superconductors
Abstract: An extensive theoretical and experimental investigation has been conducted on fermion-pair condensation and exciton condensation as distinct classes of Bose-Einstein-like condensation. In a recent Rapid Communication, the existence of a fermion-exciton condensate—a single quantum state in which the characters of both fermion-pair and exciton condensates coexist—is established computationally in the low-particle-number (N) limit and theoretically in the large-N thermodynamic limit. The trade-off between the fermion-pair and excitonic character of the fermion-exciton condensate is shown to be elliptic in nature. The possibility that the properties of fermion-exciton condensates could be a hybrid of the properties of fermion-pair condensates and exciton condensates is discussed, and future experimental and computational exploration of this class of condensate, which may potentially be realizable in a bilayer of superconductors, is anticipated.
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Volume: 2 Issue: 2 First Page #:
Date Submitted: 5/15/20 12:00AM Date Published: 4/1/20 5:00AM
Publication Location:
Article Title: Efficient two-electron ansatz for benchmarking quantum chemistry on a quantum computer
Authors: Scott E. Smart, David A. Mazziotti
Keywords: quantum computing
Abstract: Quantum chemistry provides key applications for near-term quantum computing, but these are greatly complicated by the presence of noise. In this work we present an efficient ansatz for the computation of two-electron atoms and molecules within a hybrid quantum-classical algorithm. The ansatz exploits the fundamental structure of the two-electron system, treating the nonlocal and local degrees of freedom on the quantum and classical computers, respectively. Here the nonlocal degrees of freedom scale linearly with respect to basis-set size, giving a linear ansatz with only O(1) circuit preparations required for reduced state tomography. We implement this benchmark with error mitigation on two publicly available quantum computers, calculating accurate dissociation curves for four- and six-qubit calculations of H2 and H3+.
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Article Title: Signature of van der Waals interactions in the cumulant density matrix
Authors: Olivia Werba, Alexandra Raeber, Kade Head-Marsden, David A. Mazziotti
Keywords: van der Waals
Abstract: Here we propose and implement a universal signature of the van der Waals interactions based on the cumulant part of the two-electron reduced density matrix (2-RDM). Due to the connected property of the cumulant, we can use it to detect the van der Waals interactions between two molecular moieties. In particular, we use the squared Frobenius norm of the cumulant of the 2-RDM, which has been previously shown to provide a size-extensive measure of the electron correlation. As two moieties are separated to infinity, the cumulant Frobenius norm exhibits an r?6 decay to its asymptotic limit, providing a density-based measure of the van der Waals interaction. We study this signature of van der Waals forces in a collection of small molecules of varying geometries. These computations agree with experimental trends of known literature values.
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Effect of Strong Electron Correlation in the Description and Design of Efficient Energy-Transfer Mechanisms

David Arthur Mazziotti
Department of Chemistry and The James Franck Institute
The University of Chicago, Chicago, IL 60637

I. RESEARCH ACCOMPLISHMENTS

Significant research has been accomplished uner the Army Research Office (Grant No. W911NF-16-1-0152). The research produced 40 published papers and partially supported the training of 2 postdoctoral students, 16 graduate students, and 5 undergraduate students.

1. **Towards a Resolution of the Static Correlation Problem in Density Functional Theory:** Kohn-Sham density functional theory (DFT) has long struggled with the accurate description of strongly correlated and open shell systems and improvements have been minor even in the newest hybrid functionals. We treat the static correlation in DFT when frontier orbitals are degenerate by the means of using a semidefinite programming (SDP) approach to minimize the system energy as a function of the N-representable, non-idempotent 1-electron reduced density matrix [1]. While showing greatly improved singlet-triplet gaps for linear density approximation and generalized gradient approximation (GGA) functionals, the SDP procedure reveals flaws in modern meta and hybrid GGA functionals, which show no major improvements when provided with an accurate electron density.
2. **Preparation of an Exciton Condensate on a 53-Qubit Quantum Computer:** Quantum computation promises an exponential speedup of certain classes of classical calculations through the preparation and manipulation of entangled quantum states. So far most molecular simulations on quantum computers, however, have been limited to small numbers of particles. Here we prepare a highly entangled state on a 53-qubit IBM quantum computer, representing 53 particles, which reveals the formation of an exciton condensate of photon particles and holes [2]. While elusive for more than 50 years, such condensates were recently achieved for electron-hole pairs in graphene bilayers and metal chalcogenides. Our result with a photon condensate has the potential to further the exploration of this new form of condensate that may play a significant role in realizing efficient room-temperature energy transport.
3. **Potential Coexistence of Exciton and Fermion-pair Condensations:** An extensive theoretical and experimental investigation has been conducted on fermion-pair condensation and exciton condensation as distinct classes of Bose-Einstein-like condensation. In a recent Rapid Communication, the existence of a fermion-exciton condensate—a single quantum state in which the characters of both fermion-pair and exciton condensates coexist—is established computationally in the low-particle-number (N) limit and theoretically in the large-N thermodynamic limit [3]. The trade-off between the fermion-pair and excitonic character of the fermion-exciton condensate is shown to be elliptic in nature. The possibility that the properties of fermion-exciton condensates could be a hybrid of the properties of fermion-pair condensates and exciton conden-

sates is discussed, and future experimental and computational exploration of this class of condensate, which may potentially be realizable in a bilayer of superconductors, is anticipated.

4. **Efficient Two-electron Ansatz for Benchmarking Quantum Chemistry on a Quantum Computer:** Quantum chemistry provides key applications for near-term quantum computing, but these are greatly complicated by the presence of noise. In this work we present an efficient ansatz for the computation of two-electron atoms and molecules within a hybrid quantum-classical algorithm [4]. The ansatz exploits the fundamental structure of the two-electron system, treating the nonlocal and local degrees of freedom on the quantum and classical computers, respectively. Here the nonlocal degrees of freedom scale linearly with respect to basis-set size, giving a linear ansatz with only O(1) circuit preparations required for reduced state tomography. We implement this benchmark with error mitigation on two publicly available quantum computers, calculating accurate dissociation curves for four- and six-qubit calculations of H_2 and H_3^+.
5. **Quantum Solver of Contracted Eigenvalue Equations for Scalable Molecular Simulations on Quantum Computing Devices:** The accurate computation of ground and excited states of many-fermion quantum systems is one of the most consequential, contemporary challenges in the physical and computational sciences whose solution stands to benefit significantly from the advent of quantum computing devices. Existing methodologies using phase estimation or variational algorithms have potential drawbacks such as deep circuits requiring substantial error correction or non-trivial high-dimensional classical optimization. Here we introduce a quantum solver of contracted eigenvalue equations, the quantum analogue of classical methods for the energies and reduced density matrices of ground and excited states [5]. The solver does not require deep circuits or difficult classical optimization and achieves an exponential speed-up of the exact classical algorithms. We demonstrate the algorithm though computations on both a quantum simulator and two IBM quantum processing units.
6. **Entangled Electrons Drive a non-Superexchange Mechanism in a Cobalt Quinoid Dimer Complex:** A central theme in chemistry is the understanding of the mechanisms that drive chemical transformations. A well-known, highly cited mechanism in organometallic chemistry is the superexchange mechanism in which unpaired electrons on two or more metal centers interact through an electron pair of the bridging ligand. We use a combination of novel synthesis and computation to show that such interactions may in fact occur by a more direct mechanism than superexchange that is based on direct quantum entanglement of the two metal centers [6]. Specifically, we synthesize and experimentally characterize a novel cobalt dimer complex with benzoquinoid bridging ligands and investigate its electronic structure with the variational two-electron reduced density matrix method using large active spaces. The result draws novel connections between inorganic mechanisms and quantum entanglement, thereby opening new possibilities for the design of strongly correlated organometallic compounds whose magnetic and spin properties have applications in superconductors, energy storage, thermoelectrics, and spintronics.
7. **Capturing Non-Markovian Dynamics on Near-Term Quantum Computers:** With the rapid progress in quantum hardware, there has been an increased interest

in new quantum algorithms to describe complex many-body systems searching for the still-elusive goal of 'useful quantum advantage'. Surprisingly, quantum algorithms for the treatment of open quantum systems (OQSs) have remained under-explored, in part due to the inherent challenges of mapping non-unitary evolution into the framework of unitary gates. Evolving an open system unitarily necessitates dilation into a new effective system to incorporate critical environmental degrees of freedom. In this context, we present and validate a new quantum algorithm to treat non-Markovian dynamics in OQSs built on the Ensemble of Lindblad's Trajectories approach, invoking the Sz.-Nagy dilation theorem [7]. Here we demonstrate our algorithm on the Jaynes-Cummings model in the strong coupling and detuned regimes, relevant in quantum optics and driven quantum systems studies. This algorithm, a key step towards generalized modeling of non-Markovian dynamics on a noisy-quantum device, captures a broad class of dynamics and opens up a new direction in OQS problems.

8. **Ligand Non-innocence Predicted through Quantum Entanglement:** Large-scale variational 2-RDM calculations of a vanadium oxo complex [8], a manganese superoxide dismutase mimic [9], and a nickel dithiolate [10] show that quantum entanglement stabilizes the addition of an electron to the ligands rather than the metal center, providing a quantum-mechanical explanation for ligand noninnocence. Calculations determine 2-RDMs that implicitly represent wave functions with sextillion (10^{24}) or more degrees of freedom.
9. **Molecular-scale Exciton Condensation:** We showed that a universal quantum signature for exciton condensation, a Bose-Einstein-like condensation of particle-hole pairs called excitons, can be used to both identity and quantify exciton condensation in molecular systems from direct calculations of the 2-RDM [11]. Computed large eigenvalues in the particle-hole RDMs of pentacene and hexacene electron double layers (EDLs) revealed the beginnings of condensation, suggesting the potential for exciton condensation in smaller scale molecular EDLs.
10. **Excited States from Ground-State 2-RDMs:** We developed a stable Hamiltonian-shifted regularization algorithm that dramatically improves the computation of excited-state energies from the ground-state 2-RDM [12, 13]. While single-excitation theories like configuration-interaction singles (CIS) and time-dependent density-functional-theory (TD-DFT) underestimate band gaps and excited-state splittings, the 2-RDM theory yields band gap and excited-state splittings that are in good agreement with full configuration interaction and experiment where available.
11. **Molecular Conductivity from Current-constrained 2-RDMs:** We reported a current-constrained, electronic structure-based variational principle for molecular conductivity [14, 15]. Unlike existing theories, the current-constrained variational principle determines the voltage from an electronic structure calculation of the 2-RDM in which the current is added as a constraint. We applied the variational principle to benezenedithiol where it matches experimental values and trends, improving upon previous theory by as much as 1–2 orders of magnitude.
12. **Verification of the Generalized Pauli Exclusion Principle on a Quantum Computer:** We used computations on quantum computers to experimentally verify the existence of a pure-state N-representability condition [16], also known as a generalized Pauli constraint (GPC) [17–20] Quantum many-fermion states were randomly prepared on the quantum computer and tested for constraint violations. Measure-

ments showed no violation and confirmed the GPC with an error of one part in one quintillion.

13. **Dual Formulation of the Variational 2-RDM Method:** We developed a dual formulation of the variational 2-RDM method that yields energies with D, Q, G, T1, and T2 N-representability conditions at $O(r^6)$ computational cost where r is the number of orbitals [21]. Previous methods with T1 and T2 conditions required $O(r^6)$.
14. **Pure-state N-representability Constraints on the 2-RDM:** While significant progress has been made with the ensemble N-representability conditions, not much has been previously known about the pure-state conditions on the 2-RDM. We derived the first non-trivial pure-state N-representability constraints on the 2-RDM with potential applications in quantum chemistry and condensed-matter physics [22].
15. **Non-Markovian Quantum Dynamics with Complete Positivity:** We solved the problem of performing quantum dynamics in a system with memory (non-Markovian dynamics) while keeping its density matrix positive semidefinite (complete positivity) [23–25]. We showed that a complete theory for the non-Markovian case can be developed through an extension of Lindblad's theory for Markovian dynamics through an ensemble of Lindbladian trajectories originating from different times in the system's history.
16. **Charges of Mo and Fe in Nitrogenase Cofactor, FeMoco:** FeMoco, $MoFe_7S_9C$, has been shown to be the active catalytic site for the reduction of nitrogen to ammonia in the nitrogenase protein. We performed large-scale complete active space self-consistent-field (CASSCF) variational 2-RDM calculations, using active spaces much larger than those from conventional CASSCF, to show that the charges of Mo and Fe are significantly affected by strong correlation [26]. These were the first *ab initio* calculations of FeMoco.
17. **Quantum Molecules Entangled or Disentangled with External Fields:** We showed that the electron correlation of a molecular system can be controlled through a homogeneous electric field antiparallel or parallel to the system's intrinsic dipole moment [27]. The quantum control of correlation and entanglement has potential applications in the design of molecules with tunable properties and the stabilization of qubits in quantum computations.
18. **Active-space Pair Variational 2-RDM Theory:** We developed an active-space pair variational 2-RDM theory that uses a size extensive pairing approximation to reduce the cost of solving the active space to $O(r^3)$ where r is the number of orbitals. Calculations show that the method recovers non-trivial strong electron correlation in many molecular systems. Within the approximation active spaces with hundreds of orbitals can be treated efficiently.
19. **Pseudospectral Gaussian Approach to Non-adiabatic Quantum Dynamics:** We developed a novel approach to non-adiabatic dynamics that employs pseudospectral Gaussian sampling [28, 29]. The method is important because it reduces the sampling the potential energy surfaces from quadratic to linear in the number of Gaussian wave packets.

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