Active Space Pair 2-Electron Reduced Density Matrix Theory for Strong Correlation

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Abstract

An active space variational calculation of the 2-electron reduced density matrix (2-RDM) is derived and implemented where the active orbitals are correlated within the pair approximation. The pair approximation considers only doubly occupied configurations of the wavefunction which enables the calculation of the 2-RDM at a computational cost of $O(r^3)$. Calculations were performed both with the pair active space configuration interaction (PASCI) method and the pair active space self consistent field (PASSCF) method. The latter includes a mixing of the active and inactive orbitals through unitary transformations. The active-space pair 2-RDM method is applied to the nitrogen molecule, the p-benzyne diradical, a newly synthesized BisCobalt complex, and the nitrogenase cofactor FeMoco. The FeMoco molecule is treated in a $[120,120]$ active space. Fractional occupations are recovered in each of these systems, indicating the detection and recovery of strong electron correlation.

1 Introduction

Recent work uses active space selection in conjunction with the variational 2-RDM method to capture strong electron correlation in a variety of molecules of chemical interest. An active space is a set of orbitals within the molecule that are correlated. Increasing the size of the active space alters the amount of electron correlation that can be captured with larger active spaces producing more accurate results. Because the variational 2-RDM method with the 2-positive $N$-representability conditions scales as $O(r^6)$ where $r_a$ is the number of active orbitals, it can treat much larger active spaces than conventional configuration interaction, which scales exponentially with $r_a$. To further reduce the scaling of the variational 2-RDM method, here we combine the recently developed pair variational 2-RDM method with active space methods, the pair space equivalent to both complete active space configuration interaction (CASCI) and complete active space self consistent field (CASSCF), to generate an $O(r_a^3)$ method that can efficiently treat strong correlation in molecules with the potential...
to treat significantly larger active spaces than current methods.

The doubly-occupied configuration interaction (DOCI) or pair space restricts the wavefunction to include only doubly-occupied determinants; however, in traditional wavefunction methods this approximation alone still scales exponentially with system size. While the variational 2-RDM method reduces the computational scaling to polynomial, there are also several wavefunction approximations for decreasing the doubly occupied configuration interaction scaling to polynomial such as antisymmetric product of one-reference-orbital geminals (AP1roG) and pair coupled cluster doubles (pCCD). Moreover, some work has examined active space calculations in spaces of different seniority for small molecules.

In this paper the pair variational 2-RDM theory with an active space self-consistent field (PASSCF) method is utilized where the active and inactive orbitals are iteratively rotated to decrease the energy. Combining pair methods with active-inactive orbital rotations provides an efficient approach to treating orbital rotations which have limited many pair calculations to small molecular sizes. The existing algorithms for self consistent field (SCF) in CASSCF can be utilized without modification for efficient orbital rotations. Active-active rotations, while not explicitly treated by many SCF algorithms for CASSCF, are still indirectly included through two or more active-inactive orbital rotations. We benchmark this method using the dissociation of a nitrogen dimer, a p-benzyne diradical, a recently synthesized bis-cobalt complex and a recently studied iron complex, FeMoco.

2 Theory

The energy of an $N$-electron system can be expressed as,

$$E = \sum_{ijkl} 2K_{ij}^{kl} 2D_{kl}^{ij},$$

(1)
where \(2K_{kl}^{ij}\) is the two-electron Hamiltonian given by,

\[
2K_{kl}^{ij} = \frac{4}{N-1} 1K_{k}^{i} \wedge \delta_{l}^{j} + 2V_{kl}^{ij},
\]

in which, \(1K_{k}^{i}\) and \(2V_{kl}^{ij}\) are one- and two-electron matrices containing the one- and two-electron integrals and \(\wedge\) is the Grassmann wedge product.\(^{50,53}\)

Semidefinite programming can be used to minimize the ground-state energy with respect to the 2-RDM subject to the following approximate \(N\)-representability constraints,\(^{1,4,16,20–23}\) referred to as the DQG conditions,\(^{4,7,17,17–19,45–52,54,54,55,55,56}\)

\[
\begin{align*}
2D & \succeq 0 \quad (3) \\
2Q & \succeq 0 \quad (4) \\
2G & \succeq 0, \quad (5)
\end{align*}
\]

where \(2D\), \(2Q\), and \(2G\) are the two-particle, two-hole, and particle-hole density matrices respectively whose matrix elements are defined by

\[
\begin{align*}
2D_{kl}^{ij} &= \langle \Psi | \hat{a}_i^{\dagger} \hat{a}_j^{\dagger} \hat{a}_k \hat{a}_l | \Psi \rangle \quad (6) \\
2Q_{kl}^{ij} &= \langle \Psi | \hat{a}_i \hat{a}_j \hat{a}_l^{\dagger} \hat{a}_k^{\dagger} | \Psi \rangle \quad (7) \\
2G_{kl}^{ij} &= \langle \Psi | \hat{a}_i^{\dagger} \hat{a}_j \hat{a}_l^{\dagger} \hat{a}_k | \Psi \rangle. \quad (8)
\end{align*}
\]

The variational 2-RDM method with necessary \(N\)-representability conditions is a lower-bound method in that the computed energy is a lower bound to the ground-state energy in a given finite basis set.

In the pair approximation, these three matrices take a block-diagonal form. For the 2-particle and 2-hole RDMs, these structures consist of one \(r \times r\) block and \(r\)-choose-two \(1 \times 1\)
blocks; for example, for $^2D$ they are given by:

$$
\begin{pmatrix}
\langle \hat{a}_{ia}^{\dagger} \hat{a}_{i\beta}^{\dagger} \hat{a}_{i\alpha} \rangle & \ldots & \langle \hat{a}_{ia}^{\dagger} \hat{a}_{i\beta}^{\dagger} \hat{a}_{k\alpha} \rangle \\
\vdots & \ddots & \vdots \\
\langle \hat{a}_{ka}^{\dagger} \hat{a}_{k\beta}^{\dagger} \hat{a}_{i\alpha} \rangle & \ldots & \langle \hat{a}_{ka}^{\dagger} \hat{a}_{k\beta}^{\dagger} \hat{a}_{k\alpha} \rangle
\end{pmatrix},
$$

(9)

and

$$
\begin{pmatrix}
\langle \hat{a}_{ia}^{\dagger} \hat{a}_{ja}^{\dagger} \hat{a}_{ja} \hat{a}_{ia} \rangle \\
\vdots \\
\langle \hat{a}_{ka}^{\dagger} \hat{a}_{ka}^{\dagger} \hat{a}_{ka} \hat{a}_{ka} \rangle
\end{pmatrix}.
$$

(10)

The pair structure of the particle-hole RDM is similar but slightly more complex in structure with one $r \times r$ block and $r$-choose-two $2 \times 2$ blocks given by:

$$
\begin{pmatrix}
\langle \hat{a}_{ia}^{\dagger} \hat{a}_{ia}^{\dagger} \hat{a}_{ia} \rangle & \ldots & \langle \hat{a}_{ia}^{\dagger} \hat{a}_{ia}^{\dagger} \hat{a}_{ka} \rangle \\
\vdots & \ddots & \vdots \\
\langle \hat{a}_{ka}^{\dagger} \hat{a}_{ka}^{\dagger} \hat{a}_{ia} \rangle & \ldots & \langle \hat{a}_{ka}^{\dagger} \hat{a}_{ka}^{\dagger} \hat{a}_{ka} \rangle
\end{pmatrix},
$$

(11)

and

$$
\begin{pmatrix}
\langle \hat{a}_{ia}^{\dagger} \hat{a}_{ja}^{\dagger} \hat{a}_{ja} \hat{a}_{ia} \rangle & \langle \hat{a}_{ia}^{\dagger} \hat{a}_{ja}^{\dagger} \hat{a}_{ja} \hat{a}_{ja} \rangle \\
\langle \hat{a}_{ja}^{\dagger} \hat{a}_{ja}^{\dagger} \hat{a}_{ja} \hat{a}_{ja} \rangle & \langle \hat{a}_{ja}^{\dagger} \hat{a}_{ja}^{\dagger} \hat{a}_{ja} \hat{a}_{ja} \rangle
\end{pmatrix}.
$$

(12)

With the block diagonal forms of $^2D$, $^2Q$, and $^2G$, the scaling of the pair variational 2-RDM method is $O(r^3)$.

Here, we use the pair theory within the context of an active space calculation. Performing a calculation in an active space consists of choosing $N$ electrons in $r$ orbitals to correlate while treating the remainder of the electrons and orbitals at a mean-field level of theory. Importantly, in the case of an active-space calculation the lower bound to the energy is with respect to the configuration interaction in the active space. We consider two primary active space methods within the pair variational 2-RDM framework. First, we consider a method similar to complete active space configuration interaction (CASSCF), in that the active space is computed with respect to the Hartree-Fock canonical molecular orbitals. Second, we
explore a method equivalent to the complete active space self consistent field (CASSCF) method,\textsuperscript{58} where active and inactive orbitals are iteratively rotated through a self-consistent field method. We use the second-order orbital optimization method described in Ref. \textsuperscript{59}.

The advantage of combining pair methods with active-inactive orbital rotations is that all of the existing methods for efficient rotations\textsuperscript{59} can be utilized without modification. Results indicate that this combination avoids some of the orbital optimization issues previously reported for pair theories. Furthermore, the active-inactive rotations through two or more rotations between the active and inactive orbitals indirectly include mixing of active orbitals. The computational cost of the PASIC calculation remains $O(r^3)$, while the orbital rotations in the PASSCF calculations increases the scaling to $O(r^5)$.

3 Results

In this section we will discuss our computational methodology followed by applications to the dissociation of a nitrogen dimer, a p-benzyne diradical, a newly synthesized Bis-Cobalt complex and FeMoco in Secs. 3.1, 3.2, 3.3, 3.4, and 3.5 respectively.

3.1 Computational Methodology

We have implemented the active-space pair variational 2-RDM method in the Maple Quantum Chemistry Package, an add-on package for electronic structure in the computer algebra system Maple.\textsuperscript{60,61} All calculations employ the 2-positivity (or D, Q, and G) $N$-representability conditions. The cc-pVDZ basis set is used for nitrogen and the p-benzyne diradical calculations with [10,8] and [6,6] active spaces respectively.\textsuperscript{62} The 6-31g basis set is used for the Bis-Cobalt complex calculations in a [12,10] active space.\textsuperscript{63} Finally, both STO-3G and cc-pVDZ basis sets are employed for the FeMoco calculations in [30,30], [60,60], [90,90], and [120,120] active spaces.\textsuperscript{64,65} All calculations are performed without symmetry. The occupations are the eigenvalues of the 1-RDM, the natural-orbital occupations.
3.2 Nitrogen Dissociation

The nitrogen dimer is a known example of fractional occupations as it dissociates. In Fig. 1a) we compare the variational 2-RDM CASSCF and CASSCF methods, the traditional wave function CASSCF and CASSCF methods, and the 2-RDM PASC and PASC methods. The error for the Hartree-Fock method as well as for the variational 2-RDM PASC method relative to the CASSCF energy is shown in Fig. 1b). For the same methods, the occupation numbers of the N\(_2\) dimer at 1.2 Å and 2.0 Å are shown in Table 1.

From the data in Figure 1 the approximate dissociation energy (well depth) is calculated by taking the absolute value of the difference between the energy at 2.7 Å and the equilibrium 1.1 Å. The CASSCF, 2-RDM CASSCF, and 2-RDM PASC produce dissociation energies of 325 mHartrees, 332 mHartrees, and 358 mHartrees respectively. As a point of comparison, the Hartree-Fock well depth, which is not shown in Figure 1, is 892 mHartrees. This demonstrates the pair theory’s ability to produce realistic potential energy surfaces, especially in the regions of multireference correlation.

While Figure 1a) shows that the energy recovered by the pair methods is less than that recovered by the 2-RDM or wave function CAS methods, the energy errors in Figure 1b) show that pair methods still recover a significant portion of the correlation energy. Orbital rotations in the PASC slightly decrease the energy as compared to the PASC. As the two nitrogen atoms are separated, Table 1 shows an increase in partial occupations for all methods, demonstrating the pair theory’s ability to capture strong correlation and produce accurate dissociation curves.

3.3 p-Benzyn Diradical

The Hartree-Fock, CASSCF, and both the variational 2-RDM CASSCF and PASC methods are used to calculate the lowest singlet and triplet energies for the p-benzyn diradical in the cc-pVDZ basis set as shown in Table 2. Even though the singlet is lower then the triplet experimentally by 3.8±0.3 kcal/mol, the restricted Hartree-Fock calculation predicts the
triplet to be lower than the singlet by 69.0 kcal/mol, showing that at least with correct spin symmetry all of the lowering of the singlet energy relative to the triplet energy is attributable
Table 1: The occupation numbers of N\(_2\) at 1.2 Å and 2.0 Å separation using CASCI and CASSCF, variational 2-RDM CASCI and CASSCF, and variational 2-RDM PASCI and PASSCF.

| Sep. (Å) | Wave Function | Variational 2-RDM |
|---------|---------------|-------------------|
|         | CASCI | CASSCF | CASCI | CASSCF | PASCI | PASSCF |
| 1.2     | 1.995 | 1.995 | 1.994 | 1.985 | 2.000 | 1.998 |
|         | 1.993 | 1.989 | 1.983 | 1.984 | 1.989 | 1.989 |
|         | 1.988 | 1.974 | 1.988 | 1.976 | 1.997 | 1.993 |
|         | 1.927 | 1.922 | 1.918 | 1.910 | 1.936 | 1.920 |
|         | 1.927 | 1.922 | 1.918 | 1.910 | 1.936 | 1.920 |
|         | 0.081 | 0.086 | 0.094 | 0.102 | 0.070 | 0.087 |
|         | 0.081 | 0.086 | 0.094 | 0.102 | 0.070 | 0.087 |
|         | 0.008 | 0.028 | 0.011 | 0.032 | 0.002 | 0.008 |
| 2.0     | 1.998 | 1.999 | 1.989 | 1.988 | 1.999 | 1.999 |
|         | 1.995 | 1.995 | 1.985 | 1.986 | 1.997 | 1.997 |
|         | 1.674 | 1.659 | 1.714 | 1.704 | 1.780 | 1.783 |
|         | 1.330 | 1.316 | 1.357 | 1.348 | 1.347 | 1.334 |
|         | 1.330 | 1.316 | 1.357 | 1.348 | 1.347 | 1.334 |
|         | 0.671 | 0.686 | 0.651 | 0.661 | 0.655 | 0.667 |
|         | 0.671 | 0.686 | 0.651 | 0.661 | 0.655 | 0.667 |
|         | 0.329 | 0.345 | 0.295 | 0.306 | 0.222 | 0.218 |

to electron correlation. The singlet-triplet gaps from HF, 2-RDM PASSCF, 2-RDM CASSCF (with DQG conditions), and CASSCF are -69.03, 1.26, 5.02, and 3.77 kcal/mol. These results show that the pair approximation in PASSCF captures most of the singlet state’s correlation energy that lowers its total energy below that of the triplet state. The 2-RDM PASSCF singlet-triplet gap is too small because the pair approximation does not capture all of the electron correlation while the 2-RDM CASSCF gap is slightly too large because the approximate \(N\)-representability conditions allow the singlet biradical to overcorrelate relative to the less correlated triplet state. The occupation numbers of the singlet state using the variational 2-RDM PASSCF and CASSCF methods, presented in Fig. 2, show that both methods capture the state’s biradical character, indicating that PAS is sufficient to capture the biradical character.
Table 2: The energies of p-benzyne using Hartree-Fock, CASSCF, and both the variational 2-RDM CASSCF and PASSCF methods.

|                              | Variational 2-RDM |
|------------------------------|-------------------|
|                              | HF    | CASSCF | CASSCF | PASSCF |
| Singlet Energy (Hartrees)    | -229.27 | -229.43 | -229.44 | -229.41 |
| Triplet Energy (Hartrees)    | -229.38 | -229.42 | -229.43 | -229.41 |
| Singlet-Triplet Gap (kcal/mol) | -69.03 | 3.77   | 5.02   | 1.26   |

Figure 2: Molecular orbital occupations line plot for the p-benzyne diradical using the variational 2-RDM a) CASSCF and b) PASSCF methods.

3.4 Cobalt Complex

Next, we consider a Bis-Cobalt complex \([\text{(CoTPA)}_2\text{DADT}]^{2+}\) (TPA is tris(2-pyridylmethyl)amine and DADT is 2,5-diaminobenzene-1,4-bis(thiolate)), shown in Fig. 3 that has recently been synthesized and studied. Recent work has considered the effects of different linker molecules between the cobalt centers for tuning the amount of electron correlation for a variety of potential applications.

The \(N/2\) (224) natural orbital from Hartree-Fock and variational 2-RDM PASSCF are shown in Fig. 4. The \(N/2\) natural orbital from Hartree-Fock shows significant delocalization of the orbital density over the ligands while the \(N/2\) orbital from variational 2-RDM PASSCF reveals highly localized electron density on the two metal centers, which is consistent with
the entanglement of an electron on each cobalt atom into a biradical. The occupation numbers from variational 2-RDM PASCi and PASSCF show that \( N/2 \) and \( N/2 + 1 \) natural orbitals are half-filled, confirming the existence of a biradical. The correlation energy recovered is 208 mHartrees and 384 mHartrees for the 2-RDM PASCi and PASSCF calculations respectively. The energy recovered by 2-RDM PASSCF is less than that recovered by 2-RDM CASSCF by only 6 mHartrees, revealing in this case that the pair approximation with SCF rotations recovers most of the electron correlation. The biradical character of the Bis-Cobalt complex is important to its magnetic properties, especially upon assembly into a larger crystalline solid.

### 3.5 FeMoco

Finally, we consider the modified FeMoco molecule, where the base chemical formula is \( \text{MoFe}_7\text{S}_9\text{C} \), as shown in Fig. 5. FeMoco is the active catalytic site in the reduction of
Table 3: The occupation numbers of Bis-Cobalt complex using variational 2-RDM PASCi and PASSCF with 12 electrons in 10 orbitals.

| MO Index | PASCi | PASSCF |
|----------|-------|--------|
| 223      | 2.000 | 2.000  |
| 224      | 1.063 | 1.020  |
| 225      | 0.937 | 0.980  |
| 226      | 0.000 | 0.000  |

Figure 4: Bis-cobalt complex $N/2$ (224) natural-orbital density with phases indicated by green and purple using a) Hartree-Fock and b) 2-RDM PASSCF.

nitrogen gas to ammonia during the process of nitrogen fixation.

The total energies and correlation energies for FeMoco, presented in Table 4, were calculated in the STO-3G and cc-pVDZ basis sets in [30,30], [60,60], [90,90], and [120,120] active spaces. Calculations were performed sequentially with the optimized orbitals from one active-space calculation being used to seed the orbitals of the next larger calculation. We observe that strong electron correlation is recovered in the STO-3G basis set for all active space size while it is not recovered in the cc-pVDZ basis set even for the largest active
Figure 5: Modified FeMoco molecule where Molybdenum is shown in cyan, Sulfur in yellow, Iron in brown, Oxygen in red, Nitrogen in blue, Carbon in grey, and Hydrogen in white.

While the pair approximation is sufficient to capture some of the strong correlation in FeMoco in the STO-3G basis set, it is not sufficient to capture such correlation in the larger cc-pVDZ basis set. These results are consistent with previous data on FeMoco from the variational 2-RDM method without the pair approximation. In these earlier calculations it was seen that in larger basis sets larger active spaces on the order of [20,20] are required to observe the cross-over from a nearly Hartree-Fock solution to a highly correlated solution. Here we see that it is not only the sizes of the basis set and the active space but also the degree of correlation supported by the electronic structure method that have a role in the competition between near-Hartree-Fock and strongly correlated solutions. In the larger basis set the orbitals of the Hartree-Fock solution have many degrees of freedom that lower its energy to an extent that is difficult for the correlated solution to surpass without the full flexibility of a complete, non-pairing solution of the Schrödinger equation. The application of the pair approximation to FeMoco in these two basis sets is highly instructive because it reveals the subtle but important interplay of the basis set, active space, and correlation method in treating strong electron correlation. Obtaining an accurate, correlated description of FeMoCO is important because the correlation affects properties from the atomic charges to the excited-state splittings that can influence its catalytic activity in nitrogen fixation.
Table 4: The total and correlation energies of FeMOCO in Hartrees using variational 2-RDM PASSCF using STO-3G and cc-pVDZ basis sets in [30,30], [60,60], [90,90], and [120,120] active spaces.

| Active Space | STO-3G Total Energy | STO-3G Correlation Energy | cc-pVDZ Total Energy | cc-pVDZ Correlation Energy |
|--------------|---------------------|--------------------------|----------------------|---------------------------|
| [30,30]      | -16851.44           | -0.45                    | -17030.92            | -0.20                     |
| [60,60]      | -16851.52           | -0.53                    | -17030.99            | -0.29                     |
| [90,90]      | -16851.54           | -0.55                    | -17031.06            | -0.34                     |
| [120,120]    | -16851.56           | -0.57                    | -17031.12            | -0.40                     |

4 Discussion and Conclusion

Active space variational calculations of the 2-RDM are performed where the active orbitals are correlated within the pair approximation. The pair approximation, which consists of only considering $r/2$ pairs of orbitals in the wavefunction, greatly simplifies the structure of the 2-RDM. By invoking this approximation, the computational cost of the variational calculation of the 2-RDM constrained to the 2-positive (DQG) approximate $N$-representability conditions is reduced to $O(r^3)$. Both PASCI and PASSCF calculations are considered in the treatment of $N_2$, a p-benzyne diradical, a Bis-Cobalt complex, and the nitrogenase cofactor, FeMoco. In each of these four systems, fractional occupation is observed, indicating the detection of strong electronic correlation. The pair 2-RDM theory captures a certain family of electron correlation contained within the pair approximation, which in wave function terminology is the $N$-electron Hilbert space of all doubly occupied determinants (seniority zero).

In some molecular systems the type of strong electron correlation may not be treatable within the pair approximation, such as the polyradical character in acene chains, shown in previous work, and the calculation of FeMoco in the cc-pVDZ basis set, shown here. These results are important because they not only show the limitations of pair theories in a more dramatic fashion than seen previously but also reveal the exquisite manner in which basis-set and active-spaces sizes as well as the nature of the correlation collectively play a role in determining whether the lowest-in-energy ground-state solution is nearly mean field or strongly correlated. Despite the limitations in acene chains and FeMoco the present
calculations still show that an active-space pair approximation with a self-consistent-field treatment of the inactive orbitals can capture strong electron correlation in a range of chemically relevant systems and that pair correlations have an important role in such systems. Due to the reduced computational cost and ability to capture strong correlation, the active-space pair 2-RDM methods provide a promising approach to treating molecular systems with large-scale active spaces beyond the Hartree-Fock limit.

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