A Jastrow factor coupled cluster theory for weak and strong electron correlation

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We present a Jastrow-factor-inspired variant of coupled cluster theory that accurately describes both weak and strong electron correlation. Compatibility with quantum Monte Carlo allows for variational energy evaluations and an antisymmetric geminal power reference, two features not present in traditional coupled cluster that facilitate a nearly exact description of the strong electron correlations in minimal-basis N₂ bond breaking. In double-ζ treatments of the HF and H₂O bond dissociations, where both weak and strong correlations are important, this polynomial cost method proves more accurate than either traditional coupled cluster or complete active space perturbation theory. These preliminary successes suggest a deep connection between the ways in which cluster operators and Jastrow factors encode correlation.

Predicting the effects of electron correlation remains one of the most challenging aspects of theoretical chemistry. Weak interactions and the effects of electron coalescence cusp, are small in magnitude and can be described by mean-field-based methods like coupled cluster (CC) theory. 1 The strong correlations in molecules with small gaps require methods based on other assumptions, such as active space configuration interaction 2 or the density matrix renormalization group. 3, 4 However, making accurate predictions in many important chemical systems (e.g. the oxygen evolving complex) 5 requires describing both weak and strong correlations simultaneously. This difficult goal has attracted much recent research, including developments in multi-reference CC (MRCC), 6–11 distinguishable CC, 12 quasi-variational CC, 13, 14 configuration interaction density functional theory, 15, 16 projected quasiparticle theory, 17, 18 and full configuration interaction quantum Monte Carlo (FCI-QMC). 19, 20 In the present study, we merge the strengths of CC theory, QMC Jastrow factors (JFs), and pairing functions to produce a remarkably compact ansatz that accurately describes both weak and strong correlations.

CC theory encodes correlation using energetic structure: a reference configuration is mixed with excited configurations in a size extensive way, with higher excitations becoming successively less important due to their higher energies. This energetic hierarchy lets CC truncate its excitation rank to doubles or triples while maintaining an excellent description of weak correlation. CC’s poor performance in strongly correlated systems (doubly excited states, transition metal compounds, dissociating bonds, etc.), on the other hand, is primarily a consequence of its mean-field reference, although recent work 21 shows its non-variational nature also plays a significant role.

JFs encode correlation using spatial structure via symmetric scalar functions of electron positions. 22 While this description is typically less sophisticated than CC, compatibility with QMC allows diffusion Monte Carlo (DMC) 22 to fill in the details. Indeed, real space Jastrow-Slater DMC provides an accuracy similar to CC when modeling weak correlations. 23, 24

JFs can also be constructed in Hilbert space (HS), encoding correlation via functions of the orbital occupation numbers in a localized one-electron basis. Examples include Gutzwiller factors, 25 their recent generalization to local particle number projections, 26 and some tensor networks. 27–30 Note that while real space JFs perform a similar role as explicit correlation techniques in satisfying cusp conditions, the HS-JFs used here do not, as they live entirely within the gaussian orbital basis defining the HS. In either real space or HS, JFs suppress configurations in which electrons are too close to each other, encoding correlation in a more direct (although not necessarily superior) manner than CC’s configuration interaction of energetically stratified excitations.

This report introduces a cluster-Jastrow (CJ) operator that is simultaneously a HS-JF and a simplified CC doubles operator. Its compatibility with QMC allows for variational energy evaluations at polynomial cost and for a strongly correlated antisymmetric geminal power (AGP) 17, 26, 31, 54 reference. Preliminary results in small-molecule bond breaking show that the CJ operator is a good approximation to CC doubles and that the combined CJAGP ansatz delivers accurate descriptions of both weak and strong electron correlation, at least in the relatively small basis sets accessible to our pilot implementation. These findings suggest that the traditional views of how JFs and cluster operators encode correlation may be two sides of the same coin and motivate further research into their efficient combination.

The CJAGP can be written as a CC ansatz,

\[
|\Psi\rangle = \exp(\hat{T})|\Phi\rangle,
\]

where \(\hat{T}\) is an excitation operator and \(|\Phi\rangle\) is the reference. Although the CJ could be generalized to higher excitations, doubles are typically the most important in chemistry and for now we restrict ourselves to these,

\[
\hat{T} = \sum_{\sigma, \tau \in \{\uparrow, \downarrow\}} \sum_{i,j,k,l \in [1,N]} T_{i\sigma,j\tau} a_{i\sigma}^{\dagger} a_{j\tau}^{\dagger} a_{k\sigma} a_{l\tau},
\]
where $N$ is the number of spatial orbitals and $a_k^\dagger$ creates a spin-$\uparrow$ electron in orbital $k$. By allowing all indices to range over all orbitals, we expand the typical CC excitation manifold in a way reminiscent of generalized CC \cite{CC}, which is appropriate as the AGP reference lacks any concept of occupied or virtual orbitals.

The somewhat cumbersome doubles operator is often simplified using locality-based tensor decompositions \cite{TB1, TB2, TB3} of the four-index amplitudes $T_{i_\alpha j_\beta}^{k_\gamma l_\delta}$. Here we introduce a new decomposition that makes $\hat T$ equivalent to a QMC-compatible HS-JF, enabling variational energy evaluations and an AGP reference. We define

$$T_{i_\alpha j_\beta}^{k_\gamma l_\delta} = \sum_{pq} U^*_{ip} U_{kp} J_{p_\alpha q_\beta} U^*_{jq} U_{lq}$$

where $J$ is a $2N \times 2N$ matrix of JF weights and

$$U = \exp \left( K - K^\dagger \right)$$

is a unitary one-particle rotation of HS,

$$\hat{U}^\dagger a_{i_\alpha} \hat{U} = \sum_r U_{ir} a_{r_\alpha},$$

under which $\hat T$ becomes a HS-JF,

$$\hat{J} \equiv \hat{U}^\dagger \hat{T} \hat{U} = \sum_{\sigma, \tau \in \{\uparrow, \downarrow\}} \sum_{pq} J_{p_\sigma q_\tau} a_{p_\sigma}^\dagger a_{q_\tau}^\dagger a_{q_\tau} a_{p_\sigma},$$

Note that our decomposition’s similarity to tensor hypercontraction \cite{TB4} helps explain its efficacy, although here $U$ is $N \times N$, unitary, and optimized variationally.

In addition to the cluster operator, we specify the AGP reference using its pairing matrix $F$, the vacuum $|0\rangle$, and the number of electrons $M$,

$$|\Phi\rangle = \left( \sum_{pq} F_{pq} a_{p_\downarrow}^\dagger a_{q_\uparrow}^\dagger \right)^{M/2} |0\rangle.$$  

Note that as the AGP is not related to any particular determinant, the present method differs from some MRCC approaches in that there is no dependence on a reference determinant. In total, we see that CJAGP contains only $6N^2$ variables, namely the elements of $J$, $K$, and $F$.

The HS Jastrow AGP (JAGP) \cite{JAGP} is a special case of CJAGP obtained by choosing the local orbitals in Eq. \ref{eq:agp} as the $S^{-1/2}$ Lowdin localization of the atomic orbitals. JAGP provides a qualitatively correct treatment of strong correlation, \cite{JAGP} and here we hope that the CC character of the orbital-optimized HS-JF will allow CJAGP to treat weak correlation as well.

We optimize CJAGP variationally with the function

$$E(K) = \min_{JF} \left[ \langle \Phi | e^{\hat{J}} \hat{H} e^{\hat{J}} | \Phi \rangle / \langle \Psi | \Psi \rangle \right]$$

where the second equality follows from using Eq. \ref{eq:agp}, defining $\hat{H} = \hat{U} H \hat{U}^\dagger$, and remembering that the AGP is invariant to orbital rotations. $K$ is found by a quasi-Newton L-BFGS \cite{L-BFGS} minimization of Eq. \ref{eq:agp}, during which minimizations over $J$ and $F$ are carried out by the variational Monte Carlo (VMC) linear method (LM) \cite{L-BFGS, VMC1, VMC2} for each value of $K$ that is tried. We use adjoint algorithmic differentiation \cite{L-BFGS, VMC1} to evaluate analytic derivatives of the resulting VMC estimates for $E(K)$ with respect to the transformed one- and two-electron integrals \cite{CC} that define $\hat{H}$ and to propagate these derivatives backwards through the integral transformation and Eq. \ref{eq:agp} to produce the gradient $\partial E(K)/\partial K_{ij}$. Note that the Hellman-Feynman theorem guarantees that these $\hat{H}$-routed derivatives, which like the energy may be evaluated for an $O(N^3)$ cost, \cite{L-BFGS} are the only nonzero contributions to $\partial E(K)/\partial K_{ij}$. Thus the CJAGP can be optimized variationally and at polynomial cost.

Note that we use correlated sampling \cite{correlated_sampling} to prevent statistical uncertainties from upsetting the finite differences within L-BFGS. While this approach has been sufficient for the current study, it requires sample sizes 10 to 100 times larger than for the LM alone because correlated sampling is less efficient when the two wave functions differ significantly, a common occurrence during L-BFGS line searches. In the future, we therefore hope to avoid L-BFGS and correlated sampling entirely by incorporating the optimization of $K$ directly into the LM.

Before discussing results, we describe the computational methods. One- and two-electron integrals \cite{CC} for CJAGP came from Psi3, \cite{Psi3} traditional CC results from QCChem, \cite{QCChem} and full configuration interaction (FCI) and complete active space perturbation theory (CASPT2) results from MOLPRO. \cite{CASPT2} CASPT2 active

![FIG. 1: Absolute energies in Hartrees for stretching the N2 triple bond in the STO-3G basis. Statistical uncertainties are smaller than the line width.](image)
To distinguish the effects of the CJ decomposition from those of the AGP, we have first tested a restricted Hartree-Fock (RHF) reference. This CJRHF ansatz is produced by variationally optimizing $J$ and $K$ while holding $|\Phi\rangle$ fixed as the RHF determinant, which can be written as an AGP. We see in Table I that CJRHF captures about 95% of the correlation in HF and H$_2$O at bond lengths near equilibrium in the 6-31G basis. [51] Thus, while not perfect, the CJ decomposition provides a good approximation to the full doubles operator despite its lightweight parameterization. This similarity suggests that we may interpret CC in these molecules through the JF language of suppressing the simultaneous occupation of neighboring local orbitals. This intuitive local picture of how CC encodes correlation offers an interesting complement to the traditional analyses [1] in terms of perturbation theory and diagrammatic summation.

To test CJAGP’s handling of strong correlation, we applied it to the N$_2$ triple bond stretch in a minimal STO-3G basis. [52] As seen in Table II and Figures 1 and 2, CJAGP provides an excellent description of this notoriously difficult strong correlation, [1, 21] with a non-parallelity error (NPE) (i.e. the difference between its highest and lowest errors relative to FCI) significantly smaller than those of JAGP, UCCSD(T), and CASPT2. To test our central hypothesis that the CC, JF, and AGP components of CJAGP will work together to accurately describe both weak and strong correlation, we applied it to bond stretching in HF and H$_2$O in the 6-31G basis, where both strong and a substantial amount of weak correlation will be present. Figure 2 and Table II show that in both examples, CJAGP provides a high-accuracy description of both types of correlation, outperforming UCCSD(T), JAGP, and CASPT2. These accuracies are especially remarkable considering the compactness of CJAGP: it contains $O(N^2)$ variables, compared to $O(N^4)$ for UCCSD and $O(N^4 + eN_{act})$ for CASPT2, where $N_{act}$ is the active space size.

Inspecting the optimal transformations $\hat{U}$ reveals that the local orbitals resemble atomic hybrids: sp for N$_2$ and HF and sp$^3$ for H$_2$O. We thus interpret that the CJ operator partitions molecular orbitals into chemically relevant local orbitals an then penalizes unfavorable pairwise occupations. This distills the correct superposition of resonance structures from the AGP, [34] which we believe is essential for CJAGP’s description of strong correlation.

We have presented an operator that is simultaneously a simplified cluster operator and a Jastrow factor compatible with quantum Monte Carlo methods and a geminal power reference function. In contrast to traditional coupled cluster approaches, the resulting CJAGP ansatz may be optimized variationally for a cost that scales polynomially as the fifth power of the system size, albeit with a large prefactor due to the difficulty in combining QMC

### Table I: % correlation recovered for 1 Å bonds in 6-31G.

| Method   | HF     | H$_2$O |
|----------|--------|--------|
| CJRHF    | 94.4   | 95.7   |
| CJAGP    | 99.6   | 97.5   |
| CCD      | 98.5   | 97.6   |
| CCSD     | 99.1   | 98.1   |
| CCSD(T)  | 99.7   | 98.9   |

### Table II: NPE (kcal/mol) for Figure 2

| Method       | N$_2$ | HF     | H$_2$O |
|--------------|-------|--------|--------|
| UCCSD(T)     | 6.1   | 2.1    | 5.1    |
| CASPT2       | 2.2   | 0.8    | 1.6    |
| JAGP         | 4.3   | 1.3    | 3.4    |
| CJAGP        | 0.4   | 0.3    | 1.5    |
with quasi-Newton methods. Preliminary tests show that CJAGP accurately describes both weak and strong electron correlation in small molecules, outperforming traditional coupled cluster and complete active space perturbation theory. Furthermore, the effectiveness of the cluster-Jastrow operator as a replacement for the full doubles operator reveals strong similarities between how Jastrow factors and cluster operators handle correlation.

We thank Martin Head-Gordon for many insightful discussions and for computational resources. We thank the Miller Institute for Basic Research in Science for funding.

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