Complete-Graph Tensor Network States: A New Fermionic Wave Function Ansatz for Molecules

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Abstract. We present a new class of tensor network states that are specifically designed to capture the electron correlation of a molecule of arbitrary structure. In this ansatz, the electronic wave function is represented by a Complete-Graph Tensor Network (CGTN) ansatz which implements an efficient reduction of the number of variational parameters by breaking down the complexity of the high-dimensional coefficient tensor of a full-configuration-interaction (FCI) wave function. We demonstrate that CGTN states approximate ground states of molecules accurately by comparison of the CGTN and FCI expansion coefficients. The CGTN parametrization is not biased towards any reference configuration in contrast to many standard quantum chemical methods. This feature allows one to obtain accurate relative energies between CGTN states which is central to molecular physics and chemistry. We discuss the implications for quantum chemistry and focus on the spin-state problem. Our CGTN approach is applied to the energy splitting of states of different spin for methylene and the strongly correlated ozone molecule at a transition state structure. The parameters of the tensor network ansatz are variationally optimized by means of a parallel-tempering Monte Carlo algorithm.

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1. Introduction

Over the last two decades, we have witnessed the rise of the Density Matrix Renormalization Group (DMRG) algorithm [1–3], which had a tremendous impact on the fields of condensed matter physics [4] and quantum chemistry [5, 6]. In 1995, Rommer and Östlund showed that the DMRG wave function [7, 8] can be described by a Matrix Product State (MPS) [9, 10] which is – qualitatively speaking – a one-dimensional chain of rank-3 tensors. The understanding of the structure of the DMRG wave function stimulated further developments to efficiently represent ground states of strongly correlated systems.

The work of Affleck, Kennedy, Lieb and Tasaki [11] on finitely correlated states provided the foundations of a new family of states, the tensor network states. The basic idea of tensor network states is to approximate ground-state wave functions of strongly correlated systems by spanning only the relevant part of the Hilbert space of the system of interest [12]. In the case of a limited amount of entanglement in the system, only a subspace of the full Hilbert space needs to be considered. This low-entanglement subspace can then be efficiently approximated by tensor network states tailored to represent the entanglement structure of the system.

In this article, we study a new class of approximations, which we denote Complete-Graph Tensor Network (CGTN) states, to represent electronic wave functions of molecular systems described by a complete pair-entanglement network of one-particle states (molecular orbitals). A CGTN state provides an efficient and compact description in terms of variational parameters because the 2^k expansion parameters for the many-electron states that can be constructed from k spin orbitals are approximated by the entries of a matrix symmetric in the orbital indices, i.e., only $[(k^2 - k)/2 + k] \times q^2 = k(k+1)/2 \times q^2$ parameters are needed in our CGTN approach (where q is the dimension of the one-particle Hilbert space, i.e., q=2 for spin orbitals). Of course, a detailed numerical analysis of the accuracy to approximate a total electronic state is required for this reduced parameter set. Note that an artificial one-dimensional ordering of the molecular orbitals for the construction of the total basis states, which can create convergence problems to local energy minima as in the quantum chemical DMRG algorithm [13, 14], is explicitly circumvented.

This article is organized as follows: In Section 2, we give a detailed introduction into the application of tensor network states for molecules. Afterwards, the CGTN ansatz is described in Section 3. In Section 4, the procedure for the variational optimization of the CGTN via parallel-tempering Monte Carlo is presented. The vertical spin splittings of methylene and of ozone are reported in Section 5.

2. Novel Representations of Quantum-Many Body States

The electronic Hamiltonian in second quantization reads in Hartree atomic units ('$\hbar = m_e = e = 4\pi\epsilon_0 = 1$')

$$\hat{H}_{el} = \sum_{\substack{i,j \\ \sigma}} h_{ij} a_{i\sigma}^\dagger a_{j\sigma} + \frac{1}{2} \sum_{\substack{i,j,k,l \\ \sigma,\sigma'}} V_{ijkl} a_{i\sigma}^\dagger a_{j\sigma'}^\dagger a_{k\sigma'} a_{l\sigma}, \tag{1}$$

which contains one-electron integrals h_{ij} over spatial orbitals $\phi_i(\boldsymbol{r})$ given in non-relativistic theory by [15]

$$h_{ij} = \int \phi_i^*(\boldsymbol{r}) \left(-\frac{1}{2}\nabla^2 - \sum_I \frac{Z_I}{r_I} \right) \phi_j(\boldsymbol{r}) \, d^3r, \tag{2}$$

with nuclear charge number Z_I of atomic nucleus I and electron–nucleus-I distance $r_I = |\boldsymbol{r} - \boldsymbol{R}_I|$. The nucleus–nucleus repulsion term is suppressed for the sake of brevity. The two-electron integrals V_{ijkl} are defined as

$$V_{ijkl} = \int\int \frac{\phi_i^*(\boldsymbol{r}_1)\phi_j^*(\boldsymbol{r}_2)\phi_k(\boldsymbol{r}_2)\phi_l(\boldsymbol{r}_1)}{r_{12}} \, d^3r_1 \, d^3r_2. \tag{3}$$

The Hamiltonian and its ingredients may also be written in terms of spin orbitals $\phi_i(\boldsymbol{x}) = \phi_i(\boldsymbol{r})\sigma$, where σ is a spin-up or spin-down spin eigenfunction. Coordinate $\boldsymbol{x}$ then denotes both spatial and spin variables.

The eigenstate of the electronic Hamiltonian is the total electronic wave function $|\Psi_A^{(N)}\rangle$ if we restrict ourselves to N electrons. In quantum chemistry, the full-configuration-interaction (FCI) expansion of the total electronic wave function in terms of spin-adapted configuration state functions (SU(2) eigenfunctions) exactly solves the non-relativistic time-independent Schrödinger equation in a given one-particle basis of orbitals. The FCI wave function can be understood as a linear combination of occupation number vectors in the direct-product basis of the one-particle Hilbert spaces. Occupation number vectors are generated by distributing N electrons among the k orbitals. The FCI wave function of total electronic state A then reads

$$|\Psi_{A,\mathrm{FCI}}^{(N)}\rangle = \sum_{n_1 n_2 \ldots n_k}^q C_{n_1 n_2 \ldots n_k}^{(A)} \quad |n_1 n_2 \ldots n_k\rangle \tag{4}$$

where $C_{n_1 n_2 \ldots n_k}^{(A)}$ are the (F)CI expansion coefficients of state A and $|n_1 n_2 \ldots n_k\rangle$ denotes an occupation number vector. Note that we restrict the sum in (4) to those vectors that represent N electrons and thus span the N-particle Hilbert space. The sums run over the dimension q of the local Hilbert spaces of the set of orbitals $\{1, 2, \ldots, k\}$. For spin orbitals holds $q = 2$, the occupied and unoccupied one-electron state $\{|1\rangle, |0\rangle\}$. In the case of spatial orbitals, the basis of the local Hilbert space $\{|n_i\rangle\}$ consists of four states, $\{|\rangle, |\uparrow\rangle, |\downarrow\rangle, |\uparrow\downarrow\rangle\}$. Each occupation number vector $|n\rangle \equiv |n_1 n_2 \ldots n_k\rangle$ is constructed as a direct product from the states of the local Hilbert spaces

$$|n\rangle \equiv |n_1 n_2 \ldots n_k\rangle = |n_1\rangle \otimes |n_2\rangle \otimes \ldots \otimes |n_k\rangle. \tag{5}$$

The number of variational CI parameters required to describe an electronic state (or a quantum state in general) grows exponentially with system size, which is a direct consequence of the underlying tensor-product structure of the Hilbert space.

The exponentially growing number of parameters in the FCI ansatz renders it unfeasible for molecules containing more than a few atoms. Nevertheless, because of the nature of the interactions we may hope that there exists an efficient parametrization of a class of variational wave functions such that the low-energy sector of the electronic Hamiltonian is described with sufficient accuracy [12, 16–19]. In addition, the huge body of numerical evidence compiled during the past forty to fifty years in quantum chemistry demonstrates that various truncated configuration-interaction expansions are efficient and reliable to approximate an electronic state [20]. This latter observation indicates that provided we find an efficient parametrization of all CI coefficients in the FCI expansion, we do not need to sample all occupation number vectors but only the most important ones for the total electronic energy. Otherwise, the procedure would be as unfeasible for large molecules as the FCI approach itself is.

A way of finding an efficient parametrization of states is to approximate the high-dimensional coefficient tensor $C^{(A)}_{n_1 n_2 \ldots n_k}$ by a *tensor network*. Tensor network states build a new class of variational wave functions. The high-dimensional coefficient tensor is broken down into low-rank tensors which are arranged on an arbitrary network [12, 21–27]. The primary advantage of tensor network states compared to the standard FCI expansion is the reduced number of variational parameters which approximately scales as $O(k\chi^p)$ where k is the number of orbitals, χ the bond dimension and p is the rank of the tensor. Tensor network states can be designed in a way to directly map the entanglement of the underlying system [28, 29].

The MPS constructed by the DMRG algorithm are the simplest example of tensor network states for one-dimensional systems [24, 26, 30]. An MPS with open-boundary conditions is defined as

$$|\Psi^{(N)}_{\mathrm{MPS}}\rangle = \sum_{n_1 n_2 \ldots n_k} A_1[n_1]A_2[n_2]\cdots A_k[n_k] \quad |n_1 n_2 \ldots n_k\rangle \qquad (6)$$

where the rank-3 tensors A_i are written as $m \times m$ matrices $A_i[n_i]$ for a specific local state n_i [9, 31–33]. Note that $A_1[n_1]$ and $A_k[n_k]$ are vectors because open-boundary conditions are applied and that we have dropped here and in the following the state index A for the sake of brevity. The DMRG algorithm optimizes the tensors by keeping the eigenvectors of the reduced density matrix corresponding to the dominant eigenvalues (see also McCulloch [34] and Verstraete *et al.* [12] who discussed the additional flexibility when using both wave function and Hamiltonian in MPS representation). Chan *et al.* and Hachmann *et al.* rephrased the quantum chemical DMRG algorithm consistently in terms of matrix product states [5, 35].

Other variational families of states have been proposed for strongly correlated systems which can be efficiently contracted for Variational Monte Carlo calculations. These include string-bond states (SBS) [36] and subsequently Entangled-Plaquette States (EPS) [37] and Correlator Product States (CPS) [38]. In this work, we will

build upon an extension of these families to treat the full electronic Hamiltonian for molecular systems. Our extension is twofold: (i) SBS, EPS and CPS have only been applied to local spin Hamiltonians so far, while we aim at the full electronic Hamiltonian as given in (1) and (ii) we include all pair correlations of the one-electron basis states and do not impose any restriction on these pairs.

3. Complete-Graph Tensor Network Ansatz

In the case of an MPS parametrization of a wave function, sites — or orbitals in a quantum chemical context — have to be mapped on a suitably chosen lattice. Then, correlations are transmitted over the one-dimensional lattice by the size of the matrices occurring in the matrix product state. Naturally, this ansatz is more suitable for molecular systems with an inherent linear structure rather than for those with long-range correlations. Orbital ordering on this lattice is then crucial for the convergence of the variational optimization technique employed, e.g., for the DMRG algorithm [13, 14]. Hence, an MPS state might be difficult to optimize for a general molecule of arbitrary structure. By contrast, in the CGTN approach to be introduced now non-local correlations are directly embedded into the non-linear tensor network ansatz. The Complete-Graph Tensor Network replaces the high-dimensional coefficient tensor in the FCI ansatz of (4) by a network of tensors that connects all orbitals with each other,

$$|\Psi_{\mathrm{CGTN}}^{(N)}\rangle = \sum_{n_1 n_2 \ldots n_k}^{q} \prod_{\alpha} \prod_{\beta \leq \alpha}^{k} f_{\alpha\beta}^{n_\alpha n_\beta} \quad |n_1 n_2 \ldots n_k\rangle \tag{7}$$

where $\boldsymbol{f} \equiv \{f_{\alpha\beta}^{n_\alpha n_\beta}\}$ represents a rank-$[k(k+1)/2]$ tensor which depends on the orbitals $\alpha, \beta \in \{1, 2, .., k\}$. The local states of the spin orbitals n_α, n_β can either be occupied or unoccupied $\{|1\rangle, |0\rangle\}$ (i.e., for spin orbitals $q=2$). The sum runs over all possible occupation number vectors $|n\rangle$ in the N-electron Hilbert space (in principle, in the full Fock space) with the correct number of electrons, projected spin, and point-group symmetry.

The above ansatz is built on the key idea that every orbital is "connected" with every other orbital. Hence, all CI coefficients are constructed from such pair correlations optimized for *all* orbitals. The number of variational parameters in our ansatz depends on the number of spin orbitals k and on the bond dimension d and is given as $\frac{1}{2}k(k+1)q^2$ where $d = 2$. Comparing this to the number of parameters in the FCI ansatz which scales as $O(2^k)$ for spin orbitals, it is clear that CGTN states are much more efficient in terms of the number of variational parameters. It is important to emphasize that we do not need to specify any reference configuration like in most post-Hartree–Fock methods. Our ansatz comprises naturally all basis states which can be generated in the Hilbert space of interest. Thus, although the CI coefficients are approximated by the reduced set of CGTN parameters, we can expect that CGTN calculations are (at least approximately) size-consistent.

Compared to the tensor networks suggested so far for local (spin) Hamiltonians (see last section), CGTN states form a subspace of the very general CPS parametrization, which is so general that it basically covers any non-hierarchical tensor network approximation of a wave function. In particular, they correspond to two-site CPS including all long-range correlation effects. A similar parametrization of a simple variational wave function was also chosen by Huse and Else to describe ground states of frustrated quantum spin systems [39]. However, the question arises how accurate this parametrization is for the non-local electronic Hamiltonian of (1), which shall be investigated in this work. Although undesirable from the point of view of feasibility, inaccuracies may be cured by also including three-orbital, four-orbital, ... correlations as is possible with the general CPS ansatz. Thus, we may easily increase the flexibility of CGTN states by including higher-order correlators (summing over three or more indices instead of two) or by increasing the bond dimension of the tensors from scalar values to matrices. In this work, the number of pair-correlation parameters is determined by the definition of an active orbital space, which is a standard procedure in quantum chemistry [20]. The next step is to variationally optimize the non-linear tensor network ansatz.

4. Variational Optimization

We apply a variational Monte Carlo scheme to optimize the CGTN state. In the context of tensor-network states, this was demonstrated by Schuch *et al.* [36] and by Sandvik and Vidal [40] for local Hamiltonians. We augment the optimization with a parallel tempering scheme. The energy of the system is written as an expectation value of the Hamiltonian operator over an N-electron wave function $|\Psi_{\text{CGTN}}^{(N)}\rangle$,

$$E_{\text{FCI}} = \frac{\langle\Psi_{\text{FCI}}^{(N)}|\hat{H}_{el}|\Psi_{\text{FCI}}^{(N)}\rangle}{\langle\Psi_{\text{FCI}}^{(N)}|\Psi_{\text{FCI}}^{(N)}\rangle} \leq \frac{\langle\Psi_{\text{CGTN}}^{(N)}|\hat{H}_{el}|\Psi_{\text{CGTN}}^{(N)}\rangle}{\langle\Psi_{\text{CGTN}}^{(N)}|\Psi_{\text{CGTN}}^{(N)}\rangle} \tag{8}$$

which delivers an upper bound to the exact FCI energy in a given one-particle basis.

For the sake of brevity, the tensor product in front of the occupation number vector in our CGTN ansatz is abbreviated by a scalar function C_I,

$$C_I = \langle I|\Psi_{\text{CGTN}}^{(N)}\rangle = \prod_{\alpha}^{k} \prod_{\beta \leq \alpha} f_{\alpha\beta}^{I_\alpha I_\beta} \tag{9}$$

which corresponds to a (unnormalized) CI-like coefficient for a given occupation number vector $|I\rangle$ in configuration-interaction theory,

$$|\Psi_{\text{CGTN}}^{(N)}\rangle = \sum_{I} C_I |I\rangle \tag{10}$$

Inserting (10) into the normalization integral in the denominator of (8) yields the well-known CI-like normalization condition

$$\langle\Psi_{\text{CGTN}}^{(N)}|\Psi_{\text{CGTN}}^{(N)}\rangle = \sum_{IK} C_I^\star C_K \langle I|K\rangle = \sum_{IK} C_I^\star C_K \delta_{IK} = \sum_{I} C_I^2 \tag{11}$$

where the sum takes the square of the weights over all possible basis states in the Hilbert space with correct symmetry.

We now insert (11) into (8) to get an approximation to the energy expectation value of the electronic Hamiltonian for our wave function ansatz and then substitute the ket in the denominator by (10),

$$E_{\text{approx}} = \frac{\sum_I C_I \langle \Psi_{\text{CGTN}}^{(N)} | \hat{H}_{el} | I \rangle}{\sum_I C_I^2}. \tag{12}$$

After rewriting this sum to become

$$E_{\text{approx}} = \frac{\sum_I C_I^2 \dfrac{\langle \Psi_{\text{CGTN}}^{(N)} | \hat{H}_{el} | I \rangle}{C_I}}{\sum_I C_I^2} \tag{13}$$

we can perform Monte Carlo sampling with strictly non-negative probabilities C_I^2. We define an energy estimator $E(I)$ as a function of the occupation number vector $|I\rangle$ that reads

$$E(I) \equiv \frac{\langle \Psi_{\text{CGTN}}^{(N)} | \hat{H}_{el} | I \rangle}{C_I} = \sum_J \frac{C_J}{C_I} \langle J | \hat{H}_{el} | I \rangle \tag{14}$$

For a given $|I\rangle$, the number of basis states $\langle J|$ contributing to this sum is bounded by the number of terms in the Hamiltonian. Since the occupation number vector $|I\rangle$ is not an eigenstate of the Hamiltonian, $\hat{H}_{el}|I\rangle$ produces a linear combination of occupation number vectors with coefficients constructed from the one-electron and two-electron integrals occurring in the Hamiltonian. For a molecule, the sum over J can therefore be performed exactly.

A variational optimization is in general not guaranteed to converge to a global minimum — instead, it may be trapped in local minima and yield incorrect results. In our ansatz, the highly non-linear structure and the complex energy landscape of molecules make such trapping quite likely. In particular, the approach of Sandvik and Vidal [40] which applies gradient information to propose a new set of variational parameters turns out to be unreliable in our case. We therefore use a stochastic optimization procedure that works entirely without gradient information. To each choice of variational parameters $\boldsymbol{f} = \{f_{\alpha\beta}^{n_\alpha n_\beta}\}$, we can assign an electronic energy $E(\boldsymbol{f})$. After introducing an artificial temperature T (actually, a parameter with the dimension of an energy; here measured in Hartree units, E_h), we can sample the continuous variables $\boldsymbol{f}$ following a canonical ensemble with the weight of a configuration given by $\exp(-E(\boldsymbol{f})/T)$. The limit $T \to 0$ E_h will yield the desired ground state of the molecule. It should be emphasized that this ensemble does not correspond to a physical ensemble at any finite temperature.

The advantage of this approach is that we can easily control the optimization procedure by tuning the parameter T. While an accurate simulation of the ground state is only possible for $T \to 0$ E_h that may get stuck in local minima, a simulation at larger T may easily surmount high energy barriers between local minima. We therefore

use a parallel tempering/replica exchange scheme [41] where simulations are run at several temperatures simultaneously. After a certain number of updates, replica i and replica $i+1$ at neighbouring temperatures are exchanged with a probability

$$p\left((T_i, E_i) \leftrightarrow (T_{i+1}, E_{i+1})\right) = \min\{1, \exp\left(-\Delta E/\Delta T\right)\} \qquad (15)$$

with $\Delta E = E_{i+1} - E_i$ and $\Delta T = T_{i+1}T_i/(T_i - T_{i+1})$. The set of temperatures has to be chosen in such a way that the lowest temperatures are close to $T=0$ E_h to yield information about the ground state and the highest temperatures are sufficient to overcome energy barriers. Hence, the choice depends very much on the specific problem at hand. It might be desirable to dynamically optimize the temperatures for some specific applications [42], but for the purpose of this work, we restrict ourselves to a static choice of the temperatures. For a temperature set of M temperatures in the range $[T_1, T_M]$, we choose for the remaining $M - 2$ temperatures T_l with $T_1 < T_l < T_M$:

$$T_l = T_1 \left(\exp \frac{\ln T_M - \ln T_1}{M - 1}\right)^{l-1}, \ l = 1 \ldots M. \qquad (16)$$

It is, of course, possible to finally take the state obtained from the above procedure as an input state for a direct optimization using gradient information, which may yield better accuracy close to the minimum.

5. Results

Our primary goals in this work are: (i) to analyze the CGTN ansatz for the description of electronic energies and CI coefficients of molecules and (ii) to show that we can optimize the CGTN ansatz by means of a variational parallel-tempering Monte Carlo algorithm. Our test molecules are methylene and ozone. For these small molecules we do not need to apply sampling of the occupation number vectors since the sum in (13) can be carried out explicitly. Hence, we use the above-described sampling scheme to sample the $\boldsymbol{f}$ coefficients only. As a consequence, we avoid the sampling error of the occupation number vectors and thus obtain a reliable picture of the quality of our CGTN ansatz.

5.1. Singlet and Triplet Polyatomic Radicals: The Methylene Example

The accurate calculation of different spin states is of great importance to chemistry; in particular, for chemical reactions in which a spin-crossing event occurs [43–51]. There is, however, no way to tell our optimization algorithm how to converge directly to the desired spin state. The optimization algorithm might get easily trapped in local minima corresponding to a spin-contaminated total state. One possible solution would be to sample over the basis of spin-adapted configuration state functions (CSF) which can easily be constructed as linear combinations of occupation number representations using Clebsch–Gordon coefficients producing a SU(2) eigenstate of the Hamiltonian with a well-defined total spin. In that case, however, the complete occupation number

vector basis must be constructed. Another solution, which we need to employ in our second example below, is the application of a level-shift operator as used, for instance, for the DMRG algorithm in [52]. The concept of the level-shift operator can be easily implemented in the current optimization scheme. The idea is to substitute the original Hamiltonian by an effective shifted Hamiltonian where the unwanted states with a higher multiplicity are shifted up in energy. The lowest energy state of the total system is then a spin-pure state with the correct total spin. The shifted Hamiltonian is written as

$$\hat{H}_{shifted} = \hat{H} + \epsilon \hat{S}_- \hat{S}_+ = H + \epsilon \left(\hat{S}^2 - \hat{S}_z^2 - \hat{S}_z \right) \tag{17}$$

where we add the product of the spin ladder operator to the original Hamiltonian and ϵ is a positive constant. This prevents the occurrence of states which possess the same projected spin but have a different total spin.

We choose methylene as our test molecule, for which we determine the spin splitting of the singlet and triplet states. Methylene is the smallest polyatomic radical featuring a triplet ground state and several low-lying singlet states where strong correlations effects are present [53]. We are particularly interested in the energies of the triplet ground state and the lowest-lying singlet state with point-group symmetries B_1 and A_1, respectively.

In preparatory calculations, we calculated the one-electron and two-electron integrals as well as complete-active-space (CAS) self-consistent-field (SCF) reference energies with the MOLPRO program package [54]. The orbitals have been expanded in Dunning's cc-pVTZ basis set [55, 56]. The electronic energies of the singlet and triplet state of CH_2 were studied at a C–H bond distance of 1.0753 Å and an H–C–H angle of 133.82 degrees in C_1 symmetry as reported in [53]. The integrals for the CGTN calculations are calculated over the natural orbitals of the corresponding CASSCF calculation. Within this theoretical setup, the CGTN calculations can be seen as CASCI-equivalent calculations, where the CI weights are iteratively improved rather than obtained from an expensive diagonalization step. For the parallel-tempering Monte Carlo simulation, we use eight replicas at different temperatures in the range $[1 \times 10^{-8}$ $E_h, 0.001 \, E_h]$.

We investigate three active spaces that are successively enlarged, starting with a CAS(4,4) of four spatial orbitals comprising four electrons that is increased in each step by an occupied and a virtual orbital around the Fermi level yielding in total CAS(4,4), CAS(6,6), and CAS(8,8). The CAS is specified in parentheses as (n,m) where n is the number of electrons in m molecular orbitals. The number of variational parameters in the CGTN states does not depend on the dimension of the N-particle Hilbert space but on the number of orbitals in the corresponding active space. The selected active spaces provide insight into the convergence behavior of the CGTN parametrization. For the CAS(4,4), the number of variational parameters is around three times larger than the size of the Hilbert space of CH_2 (resulting in an over-parametrization), whereas for CAS(6,6) it is of comparable size. For the CAS(8,8), however, there are about nine times more many-electron basis states (i.e., occupation number vectors) than variational parameters in the CGTN ansatz. Hence, while the first two smaller active spaces allow

us to demonstrate that the CGTN ansatz is able to reproduce the CASSCF reference, the third CAS probes the efficiency of the reduced-parameter CGTN ansatz. In order to prevent spin-contamination in the CGTN state, the energy evaluation is performed in the basis of spin-adapted configuration state functions (CSF) for the singlet and triplet calculation. The weight for the CSF is calculated as a linear combination of the weights for the occupation number vector.

In Figure 1 and Table 1, CASSCF energy splittings between singlet and triplet spin states are compared to those obtained in the CGTN calculations. The number of variational parameters are given for each calculation as well. The total absolute energies cannot be quantitatively reproduced by the CGTN states but they provide a qualitatively correct description of the energy difference between different spin states for a set of active spaces.

Figure 1. Graphical representation of the spin splitting of the singlet and triplet states of methylene with increasing size of the active space. For the singlet ($\times$) and triplet ($\square$) CGTN calculations, a spin-adapted configuration state function (CSF) basis was employed. The singlet and triplet CASSCF calculations are shown as ($+$) and ($\diamond$), respectively.
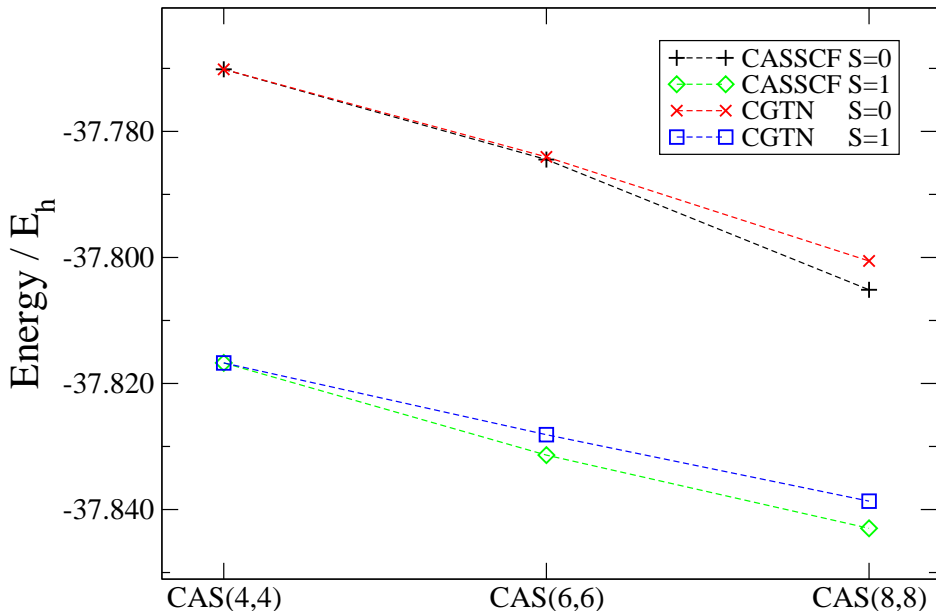
Table 1. Difference of triplet ground state and lowest-lying singlet state energies of methylene (CH_2) as obtained from CASSCF reference and CGTN calculations. The number of variational parameters in the CASSCF wave function corresponds to the number of occupation number vectors with the correct particle number and projected spin in the given active space: $\dim \mathscr{H}^{S=0}_{CASSCF}$ and $\dim \mathscr{H}^{S=1}_{CASSCF}$ parameters. The singlet and triplet states approximated by the CGTN ansatz comprise an equal number of variational parameters in the wave functions. In the last column, the difference between CASSCF and CGTN spin-splitting energies $\Delta\Delta E$ are given in kcal mol^{-1}.

CAS	$\Delta E_{CASSCF}/E_h$	$\dim \mathscr{H}^{S=0}/ \dim \mathscr{H}^{S=1}$	$\Delta E_{CGTN}/E_h$	#CGTN	$\Delta\Delta E$ / kcal mol^{-1}
(4,4)	0.0466	36/16	0.0466	144	0.0
(6,6)	0.0435	400/225	0.0441	312	-0.38
(8,8)	0.0378	4900/3136	0.0381	544	-0.18

For the CAS(4,4), the CGTN calculation exactly reproduce the CASSCF reference calculations and verify that the ansatz optimized with the parallel-tempering Monte Carlo optimization can indeed find the correct ground-state wave function. The next question to answer is whether the CGTN ansatz can also extract the essential features of the electronic structure for larger active spaces because even if total electronic energies are not well reproduced, it would be sufficient to reliably produce relative energies of chemical accuracy (of about 1 kcal mol^{-1}). We already found [52] that MPS as optimized by the DMRG algorithm can reproduce the energetical spin splitting in transition metal complexes and clusters although the one-dimensional MPS parametrization is not very suited for this problem. The energy difference between two states can converge much faster than the total electronic energies of the individual states. Considering that during a chemical process (reaction, spin flip) only a small number of orbitals is needed to qualitatively describe the changes in electronic structure, it can be understood that the parametrization of the total electronic states requires a balanced representation of all occupation number vectors that involve these orbitals. We may expect that this balanced description is possible with a CGTN ansatz. This is exactly what we observe in the CAS(6,6)- and CAS(8,8)-CGTN calculations. The relative energies appear to be better reproduced than the absolute energies for the different spin states. Even though the parametrization in terms of the CGTN states consists of only a small fraction of parameters compared to the dimension of the Hilbert space in the CAS(8,8) case, the vertical spin splitting is accurately reproduced.

The accuracy of the CGTN to represent the electronic structure can also be assessed by performing an analysis of the CI coefficients of the CASSCF and the CGTN calculations. In Figure 2 and Table 2, the CI coefficients of the ten most important occupation number vectors for the singlet and triplet CGTN and CASSCF calculations are compared.

Figure 2. The squared CI coefficients of the most important occupation number vectors are shown for the singlet (+) and triplet (◇) CASSCF and the singlet (×) and triplet (□) CGTN calculations for methylene in a CAS(8,8). Even though the CGTN state has about 90% less parameters than the CASSCF wave function, it finds the most important occupation number vectors and provides highly accurate CI coefficients.
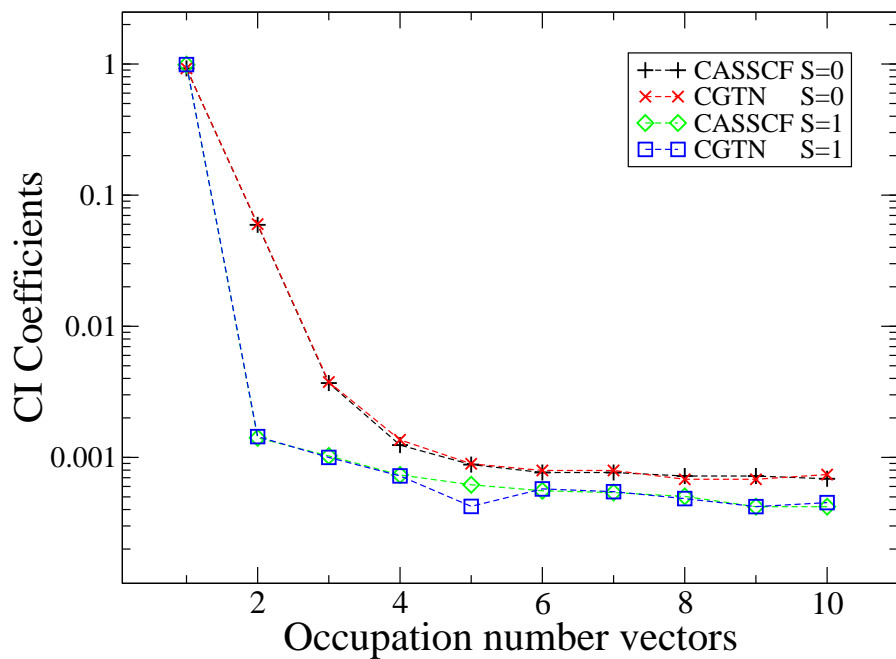
Table 2. The CI coefficients of the CASSCF and the CGTN wave functions of singlet and triplet spin symmetry are shown for the ten most important occupation number vectors. The CGTN coefficients qualitatively and even quantitatively agree with the CASSCF reference which is the exact solution for the CAS(8,8) in the given one-particle basis.

ONV	$C_{CASSCF}^{(S=0)}$	$C_{CGTN}^{(S=0)}$	$C_{CASSCF}^{(S=1)}$	$C_{CGTN}^{(S=1)}$
1	0.9623	0.9624	0.9945	0.9950
2	-0.2436	-0.2452	-0.0375	-0.0380
3	-0.0607	-0.0613	-0.0320	-0.0316
4	-0.0352	-0.0369	-0.0271	-0.0269
5	-0.0297	-0.0299	0.0249	0.0206
6	-0.0277	-0.0282	0.0236	0.0240
7	-0.0277	-0.0282	0.0232	0.0234
8	0.0269	0.0261	-0.0225	-0.0220
9	0.0269	0.0261	-0.0205	-0.0205
10	-0.0262	-0.0272	0.0205	0.0213

Qualitatively speaking, the CGTN states "carved" the important occupation number vectors out of the entire N-electron Hilbert space that characterizes the electronic structure of the underlying molecular system. Therefore, a qualitatively correct description of the electronic structure is provided by the CGTN wave function.

5.2. Strongly Correlated Molecular System: Ozone

We continue our numerical study with a most difficult case selected to probe the capabilities of the CGTN ansatz: The electronic structure of ozone at the transition state structure of the $O_2 + O$ chemical reaction is a complex multireference problem [57]. We performed CAS(8,9)-CI reference calculations for the singlet and triplet states of ozone at the transition structure reported in [57]. For this calculation, we select Dunning's cc-pVTZ basis set [55,56] and an active space consisting of the $9-14a'$ $1-3a''$ molecular orbitals. The Hilbert space of the singlet state is then spanned by 7'956 and the one for the triplet state by 5'268 occupation number vectors. The CGTN state contains only 684 variational parameters which is an efficient reduction by 91% compared to the singlet CASSCF wave function. The singlet energies of the ozone molecule at a transition state structure are given in Table 3 and show the highly multi-reference nature of the electronic structure when compared to the Hartree–Fock energy.

Table 3. Electronic energy of the singlet state of transition-state ozone in Hartree. The correlation energy (E_{corr}) denotes the energy difference between the Hartree–Fock energy and the energy obtained by a correlation method. All calculations were performed with an active space of 9 molecular orbitals comprising 8 electrons. The DMRG calculations were taken from [58] for comparison and m represents the number of many-particle DMRG system basis states. The CGTN energy for the singlet state is evaluated in a spin-adapted configuration state function (CSF) basis.

| Method	$E_{S=0}$ / E_h	E_{corr}
HF	−224.282 841	0%
CASCI	−224.384 301	100%
DMRG(m=48)	−224.384 252	99%
DMRG(m=156)	−224.384 301	100%
CGTN	−224.381 648	97%

The vertical spin splitting between the first excited singlet and ground-state triplet state is reported in Table 4. For the first excited state of singlet symmetry a CSF basis has been constructed to obtain a spin pure state withouth spin contamination. For the triplet ground state, we have tested the levelshift approach as well as no spin constrains at all and found that levelshift calculations are prone to get stuck in a local minimum. This can be circumvented if no spin constraints are applied. Then, however, spin contamination might become a problem. For the levelshift calculation, $\epsilon = 1$ was used. As in the previous study of methylene, the relative energies between the singlet and triplet states converge much faster than the total electronic energies — even for this highly multireference system. (Note that we used the same temperature range and number of replicas as in the case of methylene.)

Table 4. Vertical spin-splitting energy differences between the singlet and triplet state of ozone at the transition geometry. All calculations were in an active space of 9 molecular orbitals comprising 8 electrons. For the singlet CGTN energy, a CSF basis was employed whereas no spin constraints were imposed on the triplet state calculation.

	$E_{S=0}/E_h$	$E_{S=1}/E_h$	ΔE/kcalmol^{-1}
HF	-224.282 841	-224.357 167	46.640
CASCI	-224.384 301	-224.416 172	19.999
CGTN	-224.381 648	-224.412 775	19.532

In Figure 3, the convergence behaviour for the triplet ground state calculation is shown. It can be seen that convergence difficulties arise when the levelshift operator is applied. In the algorithm, the $\hat{S}_-\hat{S}_+$ operator translates into a high-order polynomial which features many roots and therefore many local minima.

Figure 3. The convergence of the energy for the replica with $T = 1.0 \times 10^{-8}$ E_h of the triplet CGTN state of ozone in an active space of 9 molecular orbitals and 8 electrons is shown. The inner panel shows a zoom of the first thousands Monte Carlo iterations with the Hartree–Fock and CASCI energies. It is evident that the calculation employing the levelshift operator got stuck in a local minimum. The other CGTN calculation has no spin restriction. However, since the ground state is a triplet spin state, no spin contamination is expected. This is also seen in the expectation value of the converged triplet CGTN state of $\langle \hat{S}^2 \rangle = 1.99$.
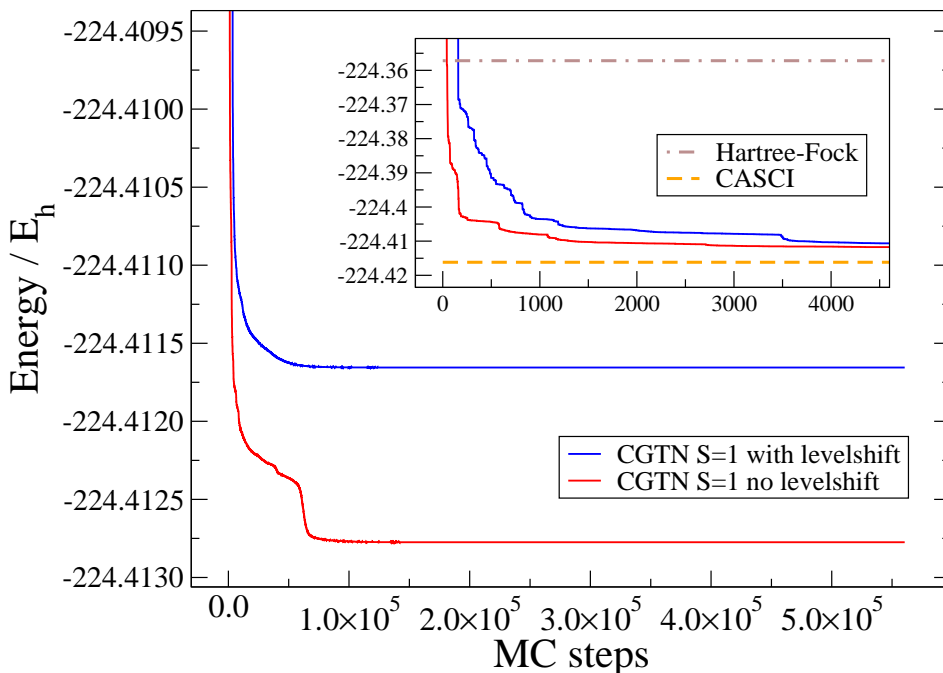
6. Conclusions

In this work, we introduced a general class of tensor network states, which we denoted Complete-Graph Tensor Network states, to approximate the electronic wave function of a molecular system. This ansatz assumes pair correlations of one-electron states (orbitals) to construct *all* CI expansion coefficients of a total electronic state. Hence, instead of 2^k — or 4^k in the case of spatial orbitals — variational parameters, we employ only $k(k + 1)/2 \times q^2$. CGTN states are a subclass of the most general CPS form of tensor network approximations to the FCI state. The accuracy of the CGTN approximation of total electronic states of molecules has been numerically studied for methylene and ozone. We should note that this is the first application of a tensor network parametrization for molecular wave functions employing the full non-local electronic many-particle Hamiltonian. For this purpose, the $k(k + 1)/2 \times q^2$ CGTN parameters have been optimized with a variational Monte Carlo protocol that we have augmented

by parallel tempering in order to prevent convergence to local minima of the electronic energy hypersurface in this parameter space.

In molecular physics and chemistry, we are primarily interested in obtaining accurate relative energies between two spin states or between two configurations on the same potential energy surface to describe the thermodynamics and kinetics of chemical reactions. The accurate calculation of relative energies is therefore mandatory. CGTN states provide the flexibility to describe electronic structures without relying on an *a priori* chosen reference configuration such as the Hartree–Fock state. The CGTN ansatz is therefore not biased to any particular Slater determinant and capable of finding the most important occupation number vectors in the Hilbert space of the molecular system.

Acknowledgments

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