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ABSTRACT

We propose a new form of Particle Number Conserving Fermionic Coherent States (PNCFCSs) that provide an efficient basis for calculating electronic wave functions. We demonstrate that a simple algorithm based on combinatorial analysis can be used for calculations of PNCFCS overlaps and matrix elements. We show an example where a basis of such coherent states with randomly selected parameters can converge quickly to the full configuration interaction result. In the future, PNCFCS can be used in dynamics just like other types of coherent states and in electronic structure theory.

Coherent states can greatly economize the basis sets that are required for accurate representation of quantum wave functions. A classical example is coherent states of harmonic oscillator, where single trajectory guided Gaussian coherent state, also known as Glauber coherent state,[1] gives exact solution of time dependent Schrödinger equation. Evolution of several coupled quantum oscillators can efficiently be described by a small basis of trajectory guided multidimensional harmonic oscillator coherent states.[2,3] This idea is behind many methods of quantum dynamics in chemistry and photochemistry. See reviews in Refs. 4–6. Coherent states of harmonic oscillator can be used also for description of bosonic systems, where in second quantization the populations and amplitudes of quantum states are represented by the amplitudes and numbers of vibrational quanta of effective harmonic oscillators. See Ref. 7 as an example of such approach. Many other types of coherent states are known,[8,9] and the approaches developed for HO CSs can be generalized.[10,11] For the purpose of this paper, we particularly mention particle number conserving bosonic CSs (PNCBCSs) and spin coherent states or coherent states of two level systems, also known as SU(2) CSs.[8,9] In the recent papers,[12,13] we also introduced a generalization of SU(2) states for fermionic systems termed as zombie states, where each spin-orbital is treated like a two level system with "dead" or "alive" states. See also the supplementary material. In this paper, we will focus on generalization of bosonic coherent states to fermionic systems and introduce Particle Number Conserving Fermionic Coherent States (PNCFCSs), for which we also work out efficient algorithm to calculate their overlap and one- and two-electron interaction matrix elements. Using a numerical example of Li_2 molecule, we demonstrate that our formalism is exact and can approach full configuration interaction result with a small number of PNCFCSs as a basis set.

Particle Number Conserving Bosonic Coherent States (PNCBCSs) are based on the standard harmonic oscillator creation and annihilation operators, also used to construct standard HO CSs. In the second quantization approach, a PNCBCS is generated as

$$|S,\boldsymbol{\xi}\rangle = |S,\xi_1,\xi_2,\ldots,\xi_M\rangle = \frac{1}{S!}\left(\sum_{i=1,M}\xi_i\hat{a}^\dagger_{Bi}\right)^S|\mathbf{0}\rangle, \tag{1}$$

where operators $\hat{a}^\dagger_{Bi}$ are the bosonic creation operators, equivalent to those of HO, and the vacuum state $|\mathbf{0}\rangle = |0,0,\ldots,0\rangle$ is a product of zero states of all M second quantization "vibrations." The overlap of such CSs is calculated very easily, as bosonic creation operators commute and (1) is a polynomial. Wave function (1) is a superposition of the states $|n_1, n_2, \ldots, n_M\rangle$ such that the total number of bosonic particles in it is by construction equal to S,

$$n_1 + n_2 + \cdots + n_M = S. \tag{2}$$

See Ref. 8 and recent applications.[10,14] How can this idea be generalized for fermions and zombie states? A straightforward replacement of bosonic operator $\hat{a}^\dagger_{Bm}$ by its fermionic counterpart $\hat{a}^\dagger_{Fm}$ in (1) yields zero due to anticommutation of fermionic operators. To avoid this problem, let us introduce a new CS as

$$|S, \boldsymbol{\xi}\rangle = |S, \xi_1, \xi_2, \ldots, \xi_M\rangle = \frac{1}{S!}\left(\sum_{m=1,M} \xi_m \hat{b}^\dagger_m\right)^S |\mathbf{0}\rangle, \tag{3}$$

where $|\mathbf{0}\rangle$ is the fermionic vacuum state and operator $\hat{b}^\dagger_m$ acts on the m-th component of zombie state in a very simple manner,

$$\hat{b}^\dagger_m|0_m\rangle = |1_m\rangle, \tag{4}$$

by creating an electron on the mth spin-orbital. Importantly, we assume that the order of creating electrons by operators $\hat{b}^\dagger_m$ does not depend on the order of operators in the product but is determined by the pre-chosen order of electronic spin-orbitals. In other words, we assume that operators $\hat{b}^\dagger_m$ and $\hat{b}^\dagger_n$ commute,

$$\left[\hat{b}^\dagger_m, \hat{b}^\dagger_n\right] = 0. \tag{5}$$

Thus, the operator $\hat{b}^\dagger_m$ is not a fermionic creation operator but can be recognized as a spin coherent state creation operator of a two-level system or a qubit creation operator that creates information about occupation. For such an operator,

$$\left(\hat{b}^\dagger_m\right)^2 = 0. \tag{6}$$

Then, Eq. (3) yields a sum of products of the first powers of operators $\hat{b}^\dagger_m$, containing all possible selections of S indices among $m = 1, \ldots, M$. As we assumed that the operators commute, their products can be arranged in the ascending order of their index m. Then, CS generated by (3) is a sum of all possible combinations of first powers of S spin-orbitals,

$$|S, \boldsymbol{\xi}\rangle = |S, \xi_1, \xi_2, \ldots, \xi_M\rangle = \sum_{m_1,<m_2<,\ldots,<m_S,} \xi_{m_1}\xi_{m_2}\ldots\xi_{m_S}[m_1, m_2, \ldots, m_S], \tag{7}$$

where $[m_1, m_2, \ldots, m_S]$ is a Slater determinant representing S occupied orbitals $m_1, m_2, \ldots, m_S$. Just like the full configuration interaction wave function, ansatz (7) contains contributions from all possible occupations of M spin-orbitals with S electrons,

$$|S, \boldsymbol{\xi}\rangle = |S, \xi_1, \xi_2, \ldots, \xi_M\rangle = \sum_{m_1,<m_2<,\ldots<m_S,} C_{m_1,m_2,\ldots,m_S}[m_1, m_2, \ldots, m_S]. \tag{8}$$

However, in (7), the coefficients $C_{m_1,m_2,\ldots,m_S}$ is factorized as

$$C_{m_1,m_2,\ldots,m_S} = \xi_{m_1}\xi_{m_2}\ldots\xi_{m_S}. \tag{9}$$

We find it convenient to annotate an $S \times S$ Slater determinant $[m_1, m_2, \ldots, m_S]$ in the form suggested in Ref. 15 as

$$[m_1, m_2, \ldots, m_S] = \begin{bmatrix} \cdots & 1 & \cdots & 1 & \cdots & 0 & \cdots & 1 & \cdots \\ \cdots & 0 & \cdots & 0 & \cdots & 1 & \cdots & 0 & \cdots \end{bmatrix}, \tag{10}$$

where a $2 \times M$ array on the right-hand side contains $\begin{bmatrix}1\\0\end{bmatrix}$ for S occupied spin-orbital in the columns $m_1, m_2, \ldots, m_S$ and $\begin{bmatrix}0\\1\end{bmatrix}$ for $M - S$ unoccupied spin-orbitals. These notations help recognize that the operator $\hat{b}^\dagger_m$ is indeed the qubit creation operator in a two level system. In addition, we can write each term in (7) as a zombie state,[12]

$$\xi_{m_1}\xi_{m_2}\ldots\xi_{m_S}[m_1, m_2, \ldots, m_S] = \begin{bmatrix} \cdots & \xi_{m_1} & \cdots & \xi_{m_2} & \cdots & 0 & \cdots & \xi_{m_S} & \cdots \\ \cdots & 0 & \cdots & 0 & \cdots & 1 & \cdots & 0 & \cdots \end{bmatrix}, \tag{11}$$

where ZS (11) contains $\begin{bmatrix}\xi_{m_i}\\0\end{bmatrix}$ for occupied spin-orbitals and $\begin{bmatrix}0\\1\end{bmatrix}$ for unoccupied spin-orbitals. See Refs. 12 and 13 and the supplementary material for a brief summary of the ZS theory and notations. A simple algorithm for calculating matrix elements between ZSs based on sign changing rule has been derived.[12]

The expression for the overlap of two PNCFCSs (7) is

$$\begin{aligned} \left\langle S, \boldsymbol{\xi}^{(a)} \middle| S, \boldsymbol{\xi}^{(b)} \right\rangle &= \sum_{m_1,<m_2<,\ldots<m_S,} \\ C^{(a)*}{}_{m_1,m_2,\ldots,m_S} C^{(b)}{}_{m_1,m_2,\ldots,m_S} &= \sum_{m_1,<m_2<,\ldots<m_S,} \left(\xi^{(a)*}{}_{m_1}\xi^{(b)}{}_{m_1}\right)\left(\xi^{(a)*}{}_{m_2}\xi^{(b)}{}_{m_2}\right)\ldots\left(\xi^{(a)*}{}_{m_S}\xi^{(b)}{}_{m_S}\right) \\ &= \sum_{m_1,<m_2<,\ldots<m_S,} (z_{m_1})(z_{m_2})\ldots(z_{m_S}), \end{aligned} \tag{12}$$

where $z_m = \xi^{(a)*}{}_m \xi^{(b)}{}_m$. Calculating sum (12) is a combinatorial problem. Consider M numbers z_m. Then, select $S < M$ numbers among them, multiply the selected numbers, and sum up over all possible selections. Such a sum can be found with the help of a generating function,

$$\prod_{i=1,M} (1 + x z_i) = \sum_{k=1,M} e_k(z_1, z_2, \ldots, z_M) x^k, \tag{13}$$

as the coefficient $e_k(z_1, z_2, \ldots, z_M)$ before the Sth power $k = S$ of x and can be calculated via the recursive formula. We have to define $e^{(k)}(n)$ to be the kth elementary symmetric sum over the first n variable $z_1, z_2, \ldots, z_n$. Then,

$$e^{(k)}(n) = e^{(k)}(n-1) + z_n e^{(k-1)}(n), \tag{14}$$

with the following base cases: $e^{(0)}(n) = 1$ for all $n \geq 0$ and $e^{(k)}(n) = 1$ for all $k < 0$ or $k > n$. See Ref. 16. Solutions (13) and (14) and Ref. 16 were found for us by the ChatGPT AI tool. Similar algorithms have been used in the antisymmetrized geminal power (AGP) theory.[17]

Now let us calculate the matrix elements of one electron interaction $\langle S, \boldsymbol{\xi}^{(b)} | \hat{a}^\dagger_{Fi} \hat{a}_{Fj} | S, \boldsymbol{\xi}^{(a)} \rangle$ between two particle number conserving fermionic CSs, where $\hat{a}^\dagger_{Fi}, \hat{a}_{Fj}$ are fermionic creation and annihilation operators. The following algorithm should be used:

(1) Get $\hat{a}_{Fj} | S, \boldsymbol{\xi}^{(a)} \rangle$ and $\hat{a}_{Fi} | S, \boldsymbol{\xi}^{(b)} \rangle$ in the form of PNCFCS by acting with an annihilation operator with sign-changing rule,[12]

$$\begin{aligned}
\hat{a}_{Fj} \left| S, \boldsymbol{\xi}^{(a)} \right\rangle &= \hat{a}_{Fj} \left| S, \xi_1^{(a)}, \ldots, \xi_j^{(a)}, \ldots, \xi_M^{(a)} \right\rangle \\
&= \xi_j^{(a)} \left| S-1, -\xi_1^{(a)}, \ldots, -\xi_{j-1}^{(a)}, 0, \xi_{j+1}^{(a)}, \ldots, \xi_M^{(a)} \right\rangle, \\
\hat{a}_{Fi} \left| S, \boldsymbol{\xi}^{(b)} \right\rangle &= \hat{a}_{Fi} \left| S, \xi_1^{(b)}, \ldots, \xi_i^{(b)}, \ldots, \xi_M^{(b)} \right\rangle \\
&= \xi_i^{(b)} \left| S-1, -\xi_1^{(b)}, \ldots, -\xi_{i-1}^{(b)}, 0, \xi_{i+1}^{(b)}, \ldots, \xi_M^{(b)} \right\rangle.
\end{aligned} \tag{15}$$

where we annihilate the electron on the spin-orbital i (or j) and also change the sign of the all parameters ξ on the left from i (or j). This is equivalent to the sign changing rule proposed in Ref. 12 to represent in zombie states approach the Jordan–Wigner factor, which appears in standard electronic structure theory where creation and annihilation operators act on the first column in Slater determinant and an additional sign factor is introduced due to the permutation of columns.[18]

(2) Using the combinatorial algorithm described above, find the matrix element $\langle S, \boldsymbol{\xi}^{(b)} | \hat{a}^\dagger_{Fi} \hat{a}_{Fj} | S, \boldsymbol{\xi}^{(a)} \rangle$ as an overlap of the two PNCFCSs (15),

$$\left\langle S, \boldsymbol{\xi}^{(b)} \middle| \hat{a}^\dagger_{Fi} \hat{a}_{Fj} \middle| S, \boldsymbol{\xi}^{(a)} \right\rangle = \xi_i^{(b)*} \xi_j^{(a)} \left\langle S-1, \boldsymbol{\xi}'^{(b)} \middle| S-1, \boldsymbol{\xi}'^{(a)} \right\rangle, \tag{16}$$

where

$$\begin{aligned}
\boldsymbol{\xi}'^{(a)} &= -\xi_1^{(a)}, \ldots, -\xi_{j-1}^{(a)}, 0, \xi_{j+1}^{(a)}, \ldots, \xi_M^{(a)}, \\
\boldsymbol{\xi}'^{(b)} &= -\xi_1^{(b)}, \ldots, -\xi_{i-1}^{(b)}, 0, \xi_{i+1}^{(b)}, \ldots, \xi_M^{(b)}.
\end{aligned} \tag{17}$$

The overlap $\langle S-1, \boldsymbol{\xi}'^{(b)} | S-1, \boldsymbol{\xi}'^{(a)} \rangle$ in (16) is calculated by the combinatorial algorithm, which chooses only $S-1$ out of M numbers. For the proof, you may think of (11) as a standard $S \times S$ Slater determinant and (7) as a sum of standard Slater determinants. Then, the operator $\hat{a}_{Fj}$ acts on the members of the sum, which contains ξ_j. Then, it moves ξ_j to the first column and adds Jordan–Wigner factor, which is equivalent to changing the sign of all $\xi_{k<j}$. The operator $\hat{a}_{Fi}$ acts similarly. Then, formula (10) becomes obvious, as the overlap is determined by all combinations of $S-1$ electrons in the columns from 2 to S. In the supplementary material, we also present another proof based on the ZS sign changing rule.[12]

The matrix elements of the two electron terms $\hat{a}^\dagger_{Fi} \hat{a}^\dagger_{Fk} \hat{a}_{Fj} \hat{a}_{Fl}$ should be calculated in a similar fashion as

$$\begin{aligned}
&\left\langle S, \boldsymbol{\xi}^{(b)} \middle| \hat{a}^\dagger_{Fi} \hat{a}^\dagger_{Fk} \hat{a}_{Fj} \hat{a}_{Fl} \middle| S, \boldsymbol{\xi}^{(a)} \right\rangle \\
&\quad = \xi_i^{(b)*} \xi_k^{(b)*} \xi_j^{(a)} \xi_l^{(a)} \left\langle S-2, \boldsymbol{\xi}''^{(b)} \middle| S-2, \boldsymbol{\xi}''^{(a)} \right\rangle,
\end{aligned} \tag{18}$$

where $\boldsymbol{\xi}''^{(a)}$ and $\boldsymbol{\xi}''^{(b)}$ are obtained from (17) by acting with another annihilation operator on $\boldsymbol{\xi}'^{(a)}$ and $\boldsymbol{\xi}'^{(b)}$. This action must again involve sign changing rule, and in (18), we calculate the overlap by combinatorial algorithm selecting only $S-2$ electrons. The proof of (18) is identical to the proof of (16).

For the Li_2 molecule described by $S = 6$ electrons on $M = 10$ spin-orbitals, we generated the basis of PNCFCSs and used the wave function

$$|\Psi\rangle = \sum_{b=1,K} A^{(b)} \left| S, \boldsymbol{\xi}^{(b)} \right\rangle. \tag{19}$$

Then, the Hamiltonian was diagonalized to obtain electronic states.

As a first test, we have reproduced MolPro[19] full CI result for 7 lowest singlet electronic states. For this, we generated a complete basis set of $K = 100$ configurations $|S, \boldsymbol{\zeta}^{(b)}\rangle$ with random amplitudes $\boldsymbol{\zeta}^{(b)}$ generated according to Gaussian distribution with mean 0 and standard deviation 1. The results are presented in Table I. One can see that the results essentially coincide with the energies given by MolPro computational package. Although this is expected considering the completeness of the basis, the results confirm that coherent states (19) can indeed be used as a basis in electronic structure calculations and that there are no mistakes in our formulas for matrix elements and overlap.

In the next step, we focused on reproducing full CI ground state energy with a significantly smaller basis set. We use the advantages of the CS approach by biasing the random amplitudes ξ_m in (3) toward what they are intuitively expected to be for the ground state. As before, we generate amplitudes according to Gaussian distribution, but now, we use mean and standard deviation both equal to 100 for two lowest orbitals, equal to 1 for the highest occupied molecular orbital, and mean 0 with deviation 0.1 for unoccupied orbitals. This choice of distribution ensures that random configurations include mostly excitations from the highest occupied orbital. As we are now interested in the ground state only, we use

TABLE I. Comparison of the energies for seven lowest singlet states of Li_2 molecule calculated using full PNCFCS basis with reference full CI energies provided my MolPro electronic structure package.

	Energies calculated with full PNCFCS basis	Reference full CI energies by MolPro	Difference
S0	−14.869 965 823 254	−14.869 965 823 579	3.248×10^{-10}
S1	−14.765 180 074 409	−14.765 180 074 491	$8.249\,93 \times 10^{-11}$
S2	−14.690 251 533 647	−14.690 251 534 192	5.451×10^{-10}
S3	−14.540 494 124 872	−14.540 494 125 236	$3.643\,01 \times 10^{-10}$
S4	−12.631 584 997 523	−12.631 584 998 860	$1.337\,4 \times 10^{-9}$
S5	−12.568 039 081 478	−12.568 039 083 831	2.353×10^{-9}
S6	−12.483 026 922 091	−12.483 026 922 131	$4.030\,02 \times 10^{-11}$

equal amplitudes for spin-up and spin-down spin-orbitals of each configuration.

Figure 1 shows the convergence of the ground state energy toward the exact full CI result as the number of configurations grows. The results are shown for four random sets of amplitudes. One can see that the convergence is sufficiently fast: while a single random configuration produces unrealistic energies in most of the cases, the results for two configurations are typically close to Hartree–Fock energy, and from 7 to 11, random configurations are required to reproduce correct full CI ground state energy. For comparison, we also include here the convergence of the regular basis set, where configurations are gradually added according to their amplitudes in the precalculated full CI vector, namely double $3 \to 4$ excitation, double $3 \to 5$ excitation, and single $3 \to 5$ excitations. As expected, the regular basis converges slightly faster for this very small system. However, due to better scaling for random basis, the PNCFCS basis approach may be more efficient for larger molecules.

We would like to emphasize that this particular way of generating amplitudes is just an example of biasing: the problem of the optimal choice of amplitudes is far beyond the scope of this paper. However, it can be easily demonstrated that a properly optimized basis set of random PNCFCSs can be at least as efficient as a regular basis. For this, we generated 100 random configurations using the same distribution for amplitudes as before and then chose the one with lowest energy. After that, we generated another 100 and chose that one that if added to the first selected gives the lowest energy of the pair. Then, we continue adding 3rd, 4th, etc., PNCFCSs in the similar way by adding the best nth basis function to the already selected basis of $n - 1$. Figure 2 shows that the random basis set optimized using the above algorithm converges even faster than a regular basis, with only 4 PNCFCSs needed to reproduce the accurate full CI ground state energy of the Li_2 molecule. Whether the above algorithm is practical for larger and more challenging systems remains

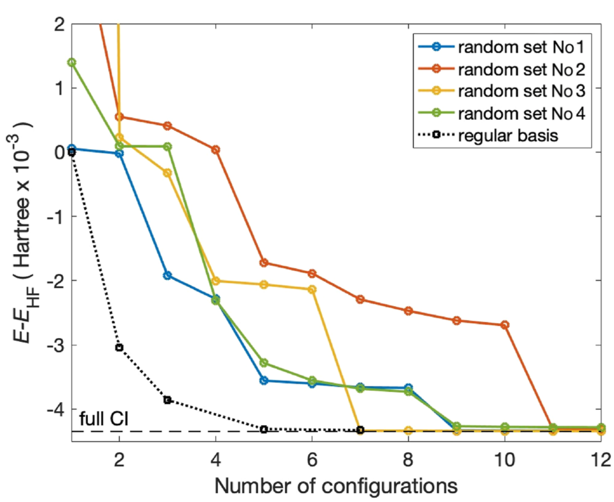

FIG. 1. Convergence of calculations with respect to the number of basis functions (19). The Hartree–Fock energy is chosen as zero. The results are given for four different sets of random amplitudes $\zeta^{(b)}$. Energy converges toward the exact full CI result very quickly. For comparison, the black curve shows the convergence of the regular basis, where we added a regular basis function already knowing their full CI contributions.

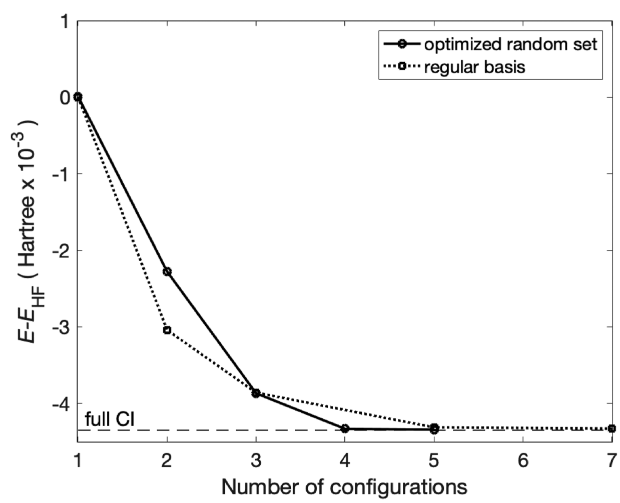

FIG. 2. Comparison of the convergence of the optimized basis set of random PNCFCSs (19) and the regular basis toward the exact full CI energy. The Hartree–Fock energy is chosen as zero.

to be seen. However, these results show that a random PNCFCS basis can, in principle, greatly economize basis sets and represent electronic wave functions very efficiently.

Our approach bares similarity to antisymmetrized geminal power (AGP),[17,20–22] used in nuclear physics,[23] electronic structure theory,[24] and theory of superconductivity where it is called number projected Bardeen–Cooper–Schrieffer (BCS) theory.[22] The AGP approach is based on the wave function ansatz $|\boldsymbol{\eta}\rangle$,

$$|AGP\rangle = |\boldsymbol{\eta}\rangle = \frac{1}{N!}\left(\sum_{i,j=1,M}\eta_{ij}\hat{S}^{\dagger}_{ij}\right)^{N}|\mathbf{0}\rangle, \tag{20}$$

where $\hat{S}^{\dagger}_{ij} = \hat{a}^{\dagger}_{Fi}\hat{a}^{\dagger}_{Fj}$ is an operator that creates a pair of electrons on spin-orbitals i and j, a geminal pair, and N is the number of geminals populated by electrons. The difference between Eqs. (20) and (3) is that the latter includes a qubit creation operator $\hat{b}^{\dagger}_{m}$ [see (4)] instead of a geminal creation operator $\hat{S}^{\dagger}_{ij}$ in the former. This reflects the fact that our approach is designed for single spin-orbitals, while AGP theory has been developed to describe strong correlated systems where electrons pair. However, operators $\hat{b}^{\dagger}_{m}$ and $\hat{S}^{\dagger}_{ij}$ have the same commutation relations, and, as a result, vast literature existing on AGP theory can be also used in our approach. This includes, for example, algorithms for calculating reduced density matrices and overlaps between AGP functions, the efficiency and stability of which is analyzed in Ref. 17.

In addition, fermionic coherent states $|\boldsymbol{\tau}\rangle$ based on Thouless's construction,[25]

$$|\boldsymbol{\tau}\rangle = \exp\left(\sum_{i=1,S}\sum_{j=S+1,M}\tau_{ij}\hat{a}^{\circ\dagger}_{i}\hat{a}^{\bullet}_{j}\right)|\boldsymbol{\Psi}_0\rangle, \tag{21}$$

have been known for quite some time and were used for description of electron dynamics.[26,27] They are generated by acting with exponential operator on the state $|\boldsymbol{\Psi}_0\rangle = |1,1,\ldots,1,0,0,\ldots,0\rangle$, where S electrons occupy the lowest spin-orbitals. Following the notation of Ref. 26, $\hat{a}^{\circ\dagger}_{i}$ and $\hat{a}^{\bullet}_{j}$ here are the operators that annihilate electron at initially populated spin-orbital j and create an electron at initially unoccupied spin-orbital i of $|\boldsymbol{\Psi}_0\rangle$. Wave function (21) is parameterized by $S\times(M-S)$ parameters τ_{ij} but similarly to (8) contains all configurations, like the full CI wave function.

As can be seen from the comparison of (3), (20), and (21), the approach proposed here is different from those of AGP and Thouless. It is a generalization of the bosonic PNCBCS[10,14] (1). Its efficiency is based on its simplicity and the use of sign changing rule combined with the combinatorial algorithm for calculating matrix elements between two PNCFCSs. We have demonstrated that the full CI result can be approached with a linear combination of a few PNCFCSs. Just like ZSs,[12,13] the new PNCFCSs allow intuitive ways of importance sampling of their parameters, but the advantage is that, unlike ZSs, the new PNCFCSs are restricted within the Fock space with the right number of electrons.

How efficient the new approach proposed in this paper will be for larger and more challenging systems remains to be seen. However, as the parameters of the basis functions $|S,\boldsymbol{\xi}^{(b)}\rangle$ were chosen randomly, the hope is that for larger molecules, this Monte Carlo based method may scale well avoiding exponential scaling.

One also can anticipate that PNCFCSs will be used in the dynamics, just like other types of CSs have been used. In this case, guiding PNCFCSs with trajectories will be vital for efficiency of quantum propagation so that the wave function ansatz will include time dependent parameters,

$$|\Psi\rangle = \sum_{b=1,K}A^{(b)}(t)\left|S,\boldsymbol{\xi}^{(b)}(t)\right\rangle. \tag{22}$$

Just like in the case of Gaussian CSs, various choice of trajectories $|S,\boldsymbol{\xi}^{(b)}(t)\rangle$ will be possible and the whole variety of methods developed for Gaussian CSs may be transferable to the case of PNCFCSs. See Ref. 28 for detailed analysis of possible trajectories to guide Gaussian coherent states. Fully variational trajectories of PNCFCSs can be obtained from variational principle applied to full wave function (22) or analytically for quadratic Hamiltonian similarly to how it has been done for number conserving bosonic coherent states.[10,14,29] "Classical" trajectories to guide the basis would follow from variational principle applied to the individual basis function[28] $|S,\boldsymbol{\xi}^{(b)}(t)\rangle$. Again, the efficiency of such an approach remains to be seen, but it is worth trying.

We derived our formalism with the help of CS generator (3) and coherent state language. However, the language is a matter of taste. In the traditional electronic structure based paradigm, we can simply start from Eqs. (8) and (9), postulate factorization of the coefficient $C_{m_1,m_2,\ldots,m_S}$, and simply use a number of such functions with different sets of parameters $\boldsymbol{\xi}$ there. Then, using an efficient algorithm for calculating overlaps and matrix elements would be the main advantage.

In summary, we propose a new type of particle number conserving fermionic coherent states as basis functions for electron dynamics and electronic structure. The simplicity of PNCFCS parameterization combined with efficient algorithms to calculate matrix elements, based on zombie states sign changing rule and combinatorics, is the key feature of the proposed approach.

The supplementary material gives a brief summary of the zombie states, sign changing rule, and provides justification of the formula (16) for matrix elements.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

Author Contributions

Dmitrii V. Shalashilin: Conceptualization (lead); Formal analysis (lead); Funding acquisition (lead); Writing – review & editing (lead). **Dmitry V. Makhov**: Data curation (lead); Software (lead); Validation (lead); Writing – review & editing (equal).

DATA AVAILABILITY

The data that support the findings of this study are available from the corresponding author upon reasonable request.

REFERENCES

[1] J. Klauder and B. Skagerstam, *Coherent States* (World Scientific, 1985).

[2] D. V. Shalashilin and M. S. Child, "The phase space CCS approach to quantum and semiclassical molecular dynamics for high-dimensional systems," Chem. Phys. **304**(1–2), 103–120 (2004).

[3] M. Ronto and D. V. Shalashilin, "Numerical implementation and test of the modified variational multiconfigurational Gaussian method for high-dimensional quantum dynamics," J. Phys. Chem. A **117**(32), 6948–6959 (2013).

[4] D. V. Makhov, C. Symonds, S. Fernandez-Alberti, and D. V. Shalashilin, "Ab initio quantum direct dynamics simulations of ultrafast photochemistry with multiconfigurational Ehrenfest approach," Chem. Phys. **493**, 200–218 (2017).

[5] B. F. E. Curchod and T. J. Martínez, "Ab initio nonadiabatic quantum molecular dynamics," Chem. Rev. **118**(7), 3305–3336 (2018).

[6] M. Ben-Nun and T. J. Martínez, *Ab Initio Quantum Molecular Dynamics*, *Advances in Chemical Physics* (John Wiley & Sons, Inc., 2002), pp. 439–512.

[7] J. A. Green and D. V. Shalashilin, "Simulation of the quantum dynamics of indistinguishable bosons with the method of coupled coherent states," Phys. Rev. A **100**(1), 013607 (2019).

[8] A. Perelomov, *Generalized Coherent States and their Applications* (Springer, Berlin, Heidelberg, 2012).

[9] P. Kramer and M. Saraceno, *Geometry of the Time-dependent Variational Principle in Quantum Mechanics* (Springer, Berlin, Heidelberg, 2014).

[10] Y. Qiao and F. Grossmann, "Exact variational dynamics of the multimode Bose–Hubbard model based SU(M) coherent states," Phys. Rev. A **103**(4), 042209 (2021).

[11] A. Grigolo, T. F. Viscondi, and M. A. M. de Aguiar, "Multiconfigurational quantum propagation with trajectory-guided generalized coherent states," J. Chem. Phys. **144**(9), 094106 (2016).

[12] D. V. Shalashilin, "Zombie states for description of structure and dynamics of multi-electron systems," J. Chem. Phys. **148**(19), 194109 (2018).

[13] O. A. Bramley, T. J. H. Hele, and D. V. Shalashilin, "Electronic energies from coupled fermionic 'Zombie' states' imaginary time evolution," J. Chem. Phys. **156**(17), 174116 (2022).

[14] Y. Qiao, J. Huh, and F. Grossmann, "Entanglement in the full state vector of boson sampling," SciPost Phys. **15**(1), 007 (2023).

[15] A. I. Streltsov, O. E. Alon, and L. S. Cederbaum, "General mapping for bosonic and fermionic operators in Fock space," Phys. Rev. A **81**(2), 022124 (2010).

[16] I. G. Macdonald, *Symmetric Functions and Hall Polynomials* (Clarendon Press, 1998).

[17] A. Khamoshi, T. M. Henderson, and G. E. Scuseria, "Efficient evaluation of AGP reduced density matrices," J. Chem. Phys. **151**(18), 184103 (2019).

[18] A. Szabo and N. S. Ostlund, *Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory* (Dover Publications, 1989).

[19] H.-J. Werner, P. J. Knowles, F. R. Manby, J. A. Black, K. Doll, A. Heßelmann, D. Kats, A. Köhn, T. Korona, D. A. Kreplin, Q. Ma, T. F. Miller III, A. Mitrushchenkov, K. A. Peterson, I. Polyak, G. Rauhut, and M. Sibaev, "The Molpro quantum chemistry package," J. Chem. Phys. **152**(14), 144107 (2020).

[20] A. J. Coleman, "The AGP model for fermion systems," Int. J. Quantum Chem. **63**(1), 23–30 (1997).

[21] A. J. Coleman and V. I. Yukalov, *Reduced Density Matrices: Coulson's Challenge* (Springer, Berlin, 2000).

[22] D. J. Rowe, "Restoration of particle number as a good quantum number in BCS theory," Nucl. Phys. A **691**(3–4), 691–709 (2001).

[23] Y. Lu, Y. Lei, C. W. Johnson, and J. J. Shen, "Nuclear states projected from a pair condensate," Phys. Rev. C **105**(3), 034317 (2022).

[24] V. N. Staroverov and G. E. Scuseria, "Optimization of density matrix functionals by the Hartree–Fock–Bogoliubov method," J. Chem. Phys. **117**(24), 11107–11112 (2002).

[25] D. J. Thouless, "Stability conditions and nuclear rotations in the Hartree–Fock theory," Nucl. Phys. **21**, 225–232 (1960).

[26] E. Deumens, A. Diz, R. Longo, and Y. Öhrn, "Time-dependent theoretical treatments of the dynamics of electrons and nuclei in molecular systems," Rev. Mod. Phys. **66**(3), 917–983 (1994).

[27] W.-M. Zhang, D. H. Feng, and R. Gilmore, "Coherent states: Theory and some applications," Rev. Mod. Phys. **62**(4), 867–927 (1990).

[28] D. V. Shalashilin and I. Burghardt, "Gaussian-based techniques for quantum propagation from the time-dependent variational principle: Formulation in terms of trajectories of coupled classical and quantum variables," J. Chem. Phys. **129**(8), 084104 (2008).

[29] Y. Qiao, F. Großmann, P. Schlagheck, and G. M. Lando, "Quantum enhancement of thermalization," Phys. Rev. Lett. **135**(6), 060404 (2025).