A new form of particle number conserving Fermionic Coherent States for electronic structure theory and electron dynamics.

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Abstract

We propose a new form of Particle Number Conserving Fermionic Coherent States (PNCFCS) which 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 future PNCFCS can be used in dynamics just like other types of Coherent States and in electronic structure theory and in electronic structure theory.

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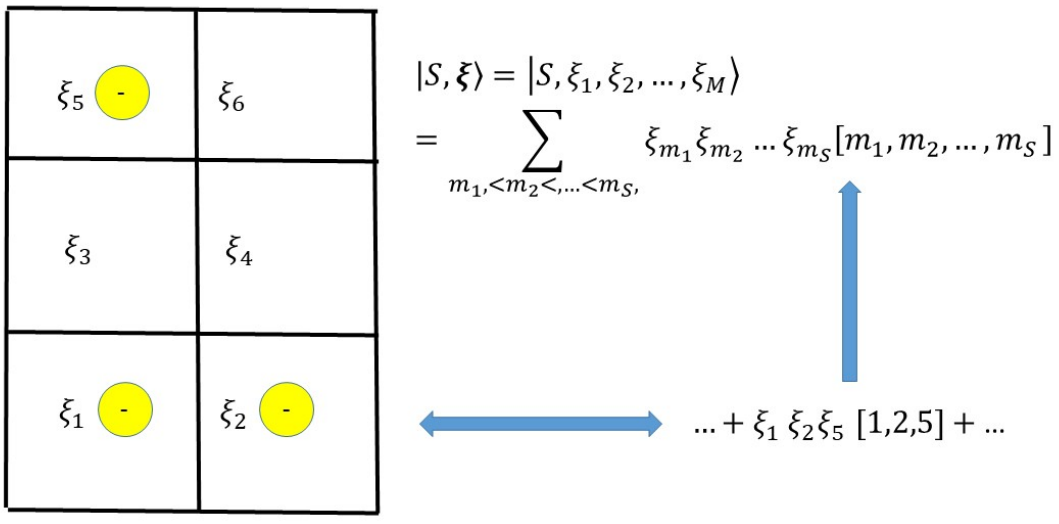

Coherent States can greatly economise the basis sets which are required for accurate representation of quantum wave functions. Classical example is Coherent States of Harmonic Oscillator, where single trajectory guided Gaussian Coherent State, also known as Glauber Coherent State[1], gives exact solution 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[4-6]. Coherent states of Harmonic Oscillator can be used also for description of Bosonic systems, where in second quantisation 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 generalised[10, 11] For the purpose of this paper we particularly mention Particle Number Conserving Bosonic CSs (PNCBCS) 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 generalisation 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 Supplementary Material. In this paper we will focus on generalisation of Bosonic Coherent States to Fermionic systems, and introduce Particle Number Conserving Fermionic Coherent States (PNCFCS), 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 PNCFCSs as a basis set.

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

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

where operators $\hat{a}_{Bi}^{\dagger}$ 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 quantisation "vibrations". The overlap of such CSs is calculated very easily, as bosonic creation operators commute and (1) is a polynomial. The 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[8] and recent applications[10, 14]. How can this idea be generalised for fermions and Zombie States? Straightforward replacement of Bosonic operator $\hat{a}_{Bm}^{\dagger}$ by its fermionic counterpart $\hat{a}_{Fm}^{\dagger}$ in (1) yields zero due to anticommutation of fermionic operators. To avoid this problem let us introduce a new CS as

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

where operator $\hat{b}_m^{\dagger}$ acts on the *m*-th component of zombie state in a very simple manner

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

by creating an electron on the *m*-th spin-orbital. Importantly we assume that the order of creating electrons by operators $\hat{b}_m^{\dagger}$ 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 $\hat{b}_m^{\dagger}$ and $\hat{b}_n^{\dagger}$ commute:

$$\left[\hat{b}_m^{\dagger}, \hat{b}_n^{\dagger}\right] = 0 \tag{5}$$

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

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

Then, eq (3) yields a sum of products of the first powers of operators $\hat{b}_m^{\dagger}$, containing all possible selections of *S* indexes among *m*=1,…,*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 1st powers of S spin-orbitals.

$$|S,\boldsymbol{\xi}\rangle = |S,\xi_1,\xi_2,\dots,\xi_M\rangle = \sum_{m_1,<m_2<,\dots<m_S,} \xi_{m_1}\xi_{m_2}\dots\xi_{m_S}[m_1,m_2,\dots,m_S] \qquad (7)$$

where $[m_1,m_2,\dots,m_S]$ is a Slater Determinant representing S occupied orbitals $m_1,m_2,\dots,m_S$. Just like the Full Configuration Interactions wave function, the ansatz (7) contains contributions from all possible occupations of M spin-orbitals with S electrons.

$$|S,\boldsymbol{\xi}\rangle = |S,\xi_1,\xi_2,\dots,\xi_M\rangle = \sum_{m_1,<m_2<,\dots<m_S,} C_{m_1,m_2,\dots,m_S}\ [m_1,m_2,\dots,m_S] \qquad (8)$$

But in (7) the coefficient $C_{m_1,m_2,\dots,m_S}$ is factorised as

$$C_{m_1,m_2,\dots,m_S} = \xi_{m_1}\xi_{m_2}\dots\xi_{m_S} \qquad (9)$$

We find it convenient to annotate $S\times S$ slater determinant $[m_1,m_2,\dots,m_S]$ in the form suggested in the ref[15] as

$$[m_1,m_2,\dots,m_S] = \begin{bmatrix}\dots & 1 & \dots & 1 & \dots & 0 & \dots & 1 & \dots\\ \dots & 0 & \dots & 0 & \dots & 1 & \dots & 0 & \dots\end{bmatrix} \qquad (10)$$

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 $m_1,m_2,\dots,m_S$ and $\begin{bmatrix}0\\1\end{bmatrix}$ for *M-S* unoccupied spin-orbitals. This notations help to recognise that operator $\hat{b}_m^\dagger$ is indeed the qubit creation operator in a two level system. Also we can write each term in (7) as a Zombie State[12]

$$\xi_{m_1}\xi_{m_2}\dots\xi_{m_S}[m_1,m_2,\dots,m_S] = \begin{bmatrix}\dots & \xi_{m_1} & \dots & \xi_{m_2} & \dots & 0 & \dots & \xi_{m_S} & \dots\\ \dots & 0 & \dots & 0 & \dots & 1 & \dots & 0 & \dots\end{bmatrix} \qquad (11)$$

where ZS (11) contains $\begin{bmatrix}\xi_{m_i}\\0\end{bmatrix}$ for occupied spin-orbital and $\begin{bmatrix}0\\1\end{bmatrix}$ for unoccupied spin-orbital. See refs[12, 13] and Supplementary Material for a brief summary of the ZS theory and notations. 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

$$\langle S,\boldsymbol{\xi}^{(a)}|S,\boldsymbol{\xi}^{(b)}\rangle = \sum_{m_1<m_2<,\ldots<m_S,}\ C^{(a)*}{}_{i_1,i_2,\ldots,i_S}\ \ C^{(b)}{}_{i_1,i_2,\ldots,i_S} =$$

$$= \sum_{m_1<m_2<,\ldots<m_S,}\left(\xi^{(a)*}{}_{m_1}\xi^{(b)}{}_{m_1}\right)\left(\xi^{(a)*}{}_{m_2}\xi^{(b)}{}_{m_2}\right)\ldots\left(\xi^{(a)*}{}_{m_S}\xi^{(b)}{}_{m_S}\right) =$$

$$= \sum_{m_1<m_2<,\ldots<m_S,}\left(z_{m_1}\right)\left(z_{m_2}\right)\ldots\left(z_{m_S}\right) \qquad (12)$$

where $z_m = \xi^{(a)*}{}_m\xi^{(b)}{}_m$. Calculating the 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 generating function

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

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

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

with 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]. The solution (13,14) and the ref[16] were found for us by 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 annihilation operator with sign-changing rule[12]

$$\hat{a}_{Fj}\left|S,\boldsymbol{\xi}^{(a)}\right\rangle = \hat{a}_{Fj}\left|S,\xi_1^{(a)},\ldots,\xi_j^{(a)},\ldots,\xi_M^{(a)}\right\rangle = \xi_j^{(a)}\left|S-1,\ -\xi_1^{(a)},\ldots,-\xi_{j-1}^{(a)},0,\xi_{j+1}^{(a)},\ldots,\xi_M^{(a)}\right\rangle$$

$$\hat{a}_{Fi}\left|S,\boldsymbol{\xi}^{(b)}\right\rangle = \hat{a}_{Fi}\left|S,\xi_1^{(b)},\ldots,\xi_i^{(b)},\ldots,\xi_M^{(b)}\right\rangle = \xi_i^{(b)}\left|S-1,\ \ -\xi_1^{(b)},\ldots,-\xi_{i-1}^{(b)},0,\xi_{i+1}^{(b)},\ldots,\xi_M^{(b)}\right\rangle$$

(15)

In (15) we annihilate the electron on the spin orbital *i* (or *j*) and also change 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 additional sign factor is introduced due to the permutation of columns.[18]

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

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

where

$$\boldsymbol{\xi}'^{(a)} = -\xi_1^{(a)},\ldots,-\xi_{j-1}^{(a)},0,\xi_{j+1}^{(a)},\ldots,\xi_M^{(a)}$$

$$\boldsymbol{\xi}'^{(b)} = -\xi_1^{(b)},\ldots,-\xi_{i-1}^{(b)},0,\xi_{i+1}^{(b)},\ldots,\xi_M^{(b)} \tag{17}$$

The overlap $\left\langle S-1,\boldsymbol{\xi}'^{(b)}\right|S-1,\boldsymbol{\xi}'^{(a)}\rangle$ in (16) is calculated by 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 determinants and (7) as a sum of standard Slater determinants. Then 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 sign of all $\xi_{k<j}$. The operator $\hat{a}_{Fi}$ acts similarly. Then the 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].

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

$$\langle S,\boldsymbol{\xi}^{(b)}|\hat{a}_{Fi}^{\dagger}\hat{a}_{Fk}^{\dagger}\,\hat{a}_{Fj}\hat{a}_{Fl}|S,\boldsymbol{\xi}^{(a)}\rangle = \xi_i^{(b)*}\xi_k^{(b)*}\xi_j^{(a)}\xi_l^{(a)}\langle S-2,\boldsymbol{\xi}''^{(b)}|S-2,\boldsymbol{\xi}''^{(a)}\rangle \quad (18)$$

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

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

Then, the Hamiltonian was diagonalised 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.

	Energies calculated with full PNCFCS basis	Reference full CI energies by MolPro	Difference
S0	-14.869965823254	-14.869965823579	3.248E-10
S1	-14.765180074409	-14.765180074491	8.24993E-11
S2	-14.690251533647	-14.690251534192	5.451E-10
S3	-14.540494124872	-14.540494125236	3.64301E-10
S4	-12.631584997523	-12.631584998860	1.3374E-09
S5	-12.568039081478	-12.568039083831	2.353E-09
S6	-12.483026922091	-12.483026922131	4.03002E-11

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.

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

Figure (1) shows the convergence of the ground state energy towards the exact Full CI result as the number of configurations grow. 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→4 excitation, double 3→5 excitation, single 3→5 excitations *etc*. 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.

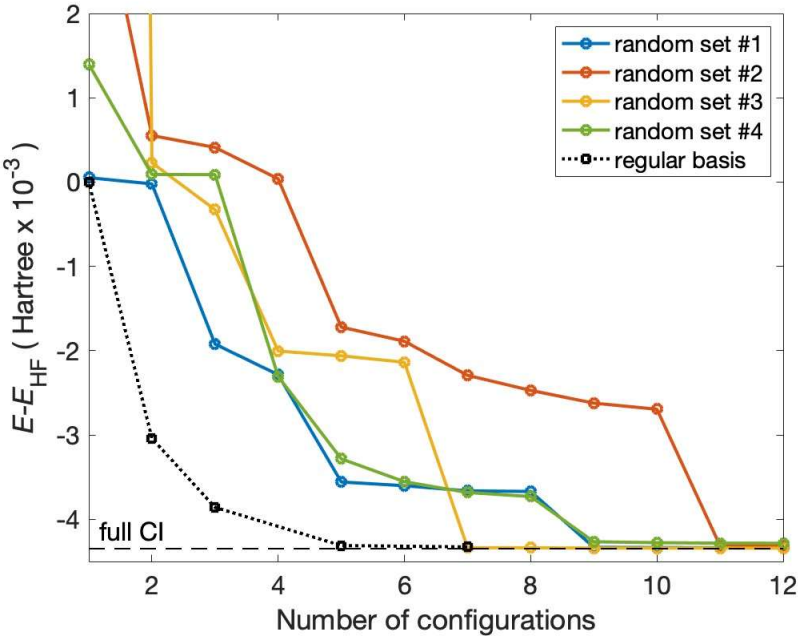

Figure 1. Convergence of calculations with respect to the number of basis functions (19). Hartree-Fock energy is chosen as zero. The results are given for four different sets of random amplitudes $\boldsymbol{\zeta}^{(b)}$. Energy converges towards the exact Full CI result very quickly. For comparison,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

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 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 choose one with lowest energy. After that, we generated another 100 and choose one which 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 *n*-th basis function to the already selected basis of *n*-1. Figure (2) shows that the random basis set optimised using the above algorithm converges even faster than a regular basis, with only 4 PNCFCSs needed to reproduce accurate full CI ground state energy of Li_2 molecule. Whether the above algorithm is practical for larger and more challenging systems remains to be seen. However, these

results shows that random PNCFCS basis can, in principle, greatly economise basis sets and represent electronic wave functions very efficiently.

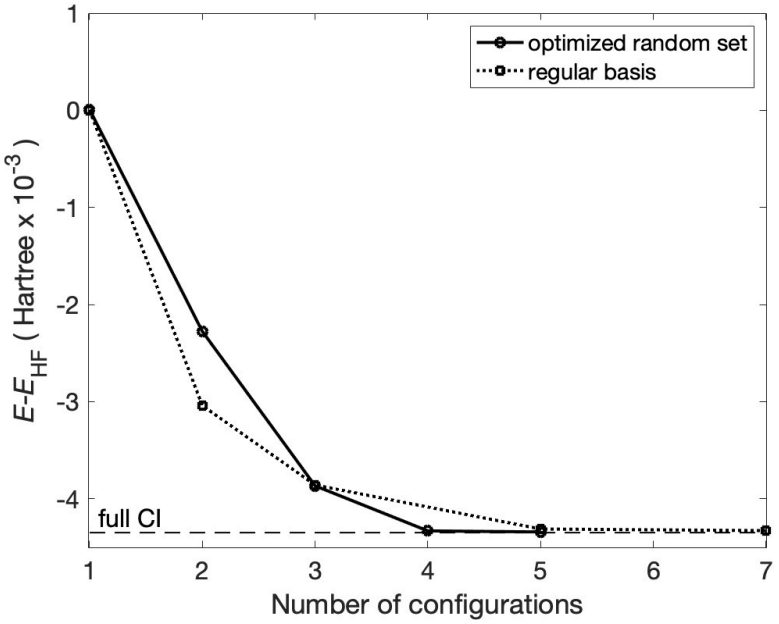

Figure 2. Comparison of the convergence of the optimised basis set of random PNCFCSs (19) and the regular basis towards the exact Full CI energy. Hartree-Fock energy is chosen as zero.

Our approach bares similarity to antisymmetrised 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-Schieffer (BCS) theory[22]. AGP approach is based on the wave function ansatz $|\boldsymbol{\eta}\rangle$

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

where $\hat{S}_{ij}^{\dagger} = \hat{a}_{Fi}^{\dagger}\hat{a}_{Fj}^{\dagger}$ is an operator which 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 qubit creation operator $\hat{b}_m^{\dagger}$ (see (4)) instead of geminal creation operator $\hat{S}_{ij}^{\dagger}$ 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 $\hat{b}_m^{\dagger}$ and $\hat{S}_{ij}^{\dagger}$ have the same commutation relations, and, as a result, vast literature existing

on AGP theory can be also used in our approach. This include, for example, algorithms for calculating reduced density matrixes and overlaps between AGP functions, efficiency and stability of which is analysed in the ref[17].

Also Fermionic Coherent States $|\boldsymbol{\tau}\rangle$ based on Thouless's construction[25]

$$|\boldsymbol{\tau}\rangle = \exp\left(\sum_{i=1,S}\sum_{j=S+1,M}\ \tau_{ij}\hat{a}_i^{\circ\dagger}\hat{a}_j^{\bullet}\right)|\boldsymbol{\Psi_0}\rangle \qquad (21)$$

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 $|\boldsymbol{\Psi_0}\rangle = |1,1,\dots,1,0,0,\dots,0\rangle$, where S electrons occupy the lowest spin-orbitals. Following the notation of the ref[26], $\hat{a}_i^{\circ\dagger}$ and $\hat{a}_j^{\bullet}$ here are the operators which annihilate electron at initially populated spin-orbital j and create an electron at initially unoccupied spin orbital i of $|\boldsymbol{\Psi_0}\rangle$. The wave function (21) is parametrised by $S \times (M - S)$ parameters τ_{ij} but similarly to (8) contains all configurations, like full CI wave function.

As can be seen from comparison of (3), (20) and (21), the approach proposed here is different from those of AGP and Thouless. It is a generalisation of the Bosonic PNCBCS[10, 14] (1). Its efficiency is based on its simplicity and the use of sign changing rule combined with combinatorial algorithm for calculating matrix elements between two PNCFCSs. We have demonstrated that 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 $\left|S, \boldsymbol{\xi}^{(b)}\right\rangle$ 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

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

Just like in the case of Gaussian CSs various choice of trajectories $\left|S,\boldsymbol{\xi}^{(b)}(t)\right\rangle$ 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 the 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 individual basis function[28] $\left|S,\boldsymbol{\xi}^{(b)}(t)\right\rangle$. Again, the efficiency of such an approach remains to be seen but it is worth trying.

We derived our formalism with the help of the CS generator (3) and Coherent States language. But the language is a matter of taste. In the traditional electronic structure based paradigm we can simply start from Eqs(8) and (9), postulate factorisation 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 efficient combinatorial 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 parametrisation combined with efficient algorithms to calculate matrix elements, based on Zombie States sign changing rule and combinatorics, are the key feature of the proposed approach.

Data Availability

The data is available from the corresponding author upon reasonable request.

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References

1. Klauder, J.; Skagerstam, B., *Coherent States*. World Scientific: 1985.
2. Shalashilin, D. V.; Child, M. S., The phase space CCS approach to quantum and semiclassical molecular dynamics for high-dimensional systems. *Chemical Physics* **2004,** *304* (1–2), 103-120.
3. Ronto, M.; Shalashilin, D. V., Numerical Implementation and Test of the Modified Variational Multiconfigurational Gaussian Method for High-Dimensional Quantum Dynamics. *The Journal of Physical Chemistry A* **2013,** *117* (32), 6948-6959.
4. Makhov, D. V.; Symonds, C.; Fernandez-Alberti, S.; Shalashilin, D. V., Ab initio quantum direct dynamics simulations of ultrafast photochemistry with Multiconfigurational Ehrenfest approach. *Chemical Physics* **2017,** *493*, 200-218.
5. Curchod, B. F. E.; Martínez, T. J., Ab Initio Nonadiabatic Quantum Molecular Dynamics. *Chemical Reviews* **2018,** *118* (7), 3305-3336.
6. Ben-Nun, M.; Martínez, T. J., Ab Initio Quantum Molecular Dynamics. In *Advances in Chemical Physics*, John Wiley & Sons, Inc.: 2002; pp 439-512.
7. Green, J. A.; Shalashilin, D. V., Simulation of the quantum dynamics of indistinguishable bosons with the method of coupled coherent states. *Physical Review A* **2019,** *100* (1), 013607.
8. Perelomov, A., *Generalized Coherent States and Their Applications*. Springer Berlin Heidelberg: 2012.
9. Kramer, P.; Saraceno, M., *Geometry of the Time-Dependent Variational Principle in Quantum Mechanics*. Springer Berlin Heidelberg: 2014.
10. Qiao, Y.; Grossmann, F., Exact variational dynamics of the multimode Bose-Hubbard model based SU(M) coherent states. *Physical Review A* **2021,** *103* (4), 042209.
11. Grigolo, A.; Viscondi, T. F.; de Aguiar, M. A. M., Multiconfigurational quantum propagation with trajectory-guided generalized coherent states. *The Journal of Chemical Physics* **2016,** *144* (9).
12. Shalashilin, D. V., Zombie states for description of structure and dynamics of multi-electron systems. *Journal of Chemical Physics* **2018,** *148* (19), 194109.
13. Bramley, O. A.; Hele, T. J. H.; Shalashilin, D. V., Electronic energies from coupled fermionic "Zombie" states' imaginary time evolution. *The Journal of Chemical Physics* **2022,** *156* (17).
14. Qiao, Y.; Huh, J.; Grossmann, F., Entanglement in the full state vector of boson sampling. *SciPost Physics* **2023,** *15* (007).
15. Streltsov, A. I.; Alon, O. E.; Cederbaum, L. S., General mapping for bosonic and fermionic operators in Fock space. *Physical Review A* **2010,** *81* (2), 12.
16. Macdonald, I. G., *Symmetric Functions and Hall Polynomials*. Clarendon Press: 1998.
17. Khamoshi, A.; Henderson, T. M.; Scuseria, G. E., Efficient evaluation of AGP reduced density matrices. *The Journal of Chemical Physics* **2019,** *151* (18).
18. Szabo, A.; Ostlund, N. S., *Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory*. Dover Publications: 1989.
19. Werner, H.-J.; Knowles, P. J.; Manby, F. R.; Black, J. A.; Doll, K.; Heßelmann, A.; Kats, D.; Köhn, A.; Korona, T.; Kreplin, D. A.; Ma, Q.; Miller, T. F., III; Mitrushchenkov, A.; Peterson, K. A.; Polyak, I.; Rauhut, G.; Sibaev, M., The Molpro quantum chemistry package. *The Journal of Chemical Physics* **2020,** *152* (14).
20. Coleman, A. J., The AGP model for fermion systems. **1997,** *63* (1), 23-30.
21. Coleman, A. J.; Yukalov, V. I., *Reduced density matrices : Coulson's challenge*. Springer: Berlin, 2000.
22. Rowe, D. J., Restoration of particle number as a good quantum number in BCS theory. *Nuclear Physics A* **2001,** *691* (3), 691-709.
23. Lu, Y.; Lei, Y.; Johnson, C. W.; Shen, J. J., Nuclear states projected from a pair condensate. *Physical Review C* **2022,** *105* (3), 034317.

24. Staroverov, V. N.; Scuseria, G. E., Optimization of density matrix functionals by the Hartree–Fock–Bogoliubov method. *The Journal of Chemical Physics* **2002,** *117* (24), 11107-11112.
25. Thouless, D. J., Stability conditions and nuclear rotations in the Hartree-Fock theory. *Nuclear Physics* **1960,** *21*, 225-232.
26. Deumens, E.; Diz, A.; Longo, R.; Öhrn, Y., Time-dependent theoretical treatments of the dynamics of electrons and nuclei in molecular systems. *Reviews of Modern Physics* **1994,** *66* (3), 917-983.
27. Zhang, W.-M.; Feng, D. H.; Gilmore, R., Coherent states: Theory and some applications. *Reviews of Modern Physics* **1990,** *62* (4), 867-927.
28. Shalashilin, D. V.; Burghardt, I., Gaussian-based techniques for quantum propagation from the time-dependent variational principle: Formulation in terms of trajectories of coupled classical and quantum variables. **2008,** *129* (8), 084104.
29. Qiao, Y.; Großmann, F.; Schlagheck, P.; Lando, G. M., Quantum Enhancement of Thermalization. *Physical Review Letters* **2025,** *135* (6), 060404.

Supplementary Material.

Zombie States, Sign Changing rule, and justification of the formula for matrix elements

As mentioned in the Discussion and Conclusions section, the proposed approach can be derived without the Coherent States language but personally we found this language productive. Our thinking was based on the Zombie States[1], which we outline here for convenience. The term Zombie State (ZS) refers to a superposition of "dead" or "alive" states $|1_m\rangle$ and $|0_m\rangle$, which describe an occupied or unoccupied spin-orbital *m.*

$$|\zeta_m(a_{1m}, a_{0m})\rangle = a_{1m}|1_m\rangle + a_{0m}|0_m\rangle \quad \text{(S1)}$$

Zombie States are similar to the SU(2) coherent states of a two levels system[2]. In SU(2) states one of the coefficients is usually assumed to be real, but it does not have to be. Both a_{0m} and a_{1m} can be complex, which would introduce an insignificant phase factor. (S1) is sometimes also called Bogoliubov quasiparticle. For multi-electronic system we associate a ZS with each spin-orbital, so that there are *M* simultaneously "dead" and "alive" Zombie electrons, one at each of the *M* spin-orbital. Let us write an *M*-particle ZS as an antisymmetrised product of *M* single particle/single orbit ZSs, or a Slater determinant made of *M* one electron Zombie States$|\zeta_m\rangle$:

$$|\boldsymbol{\zeta}\rangle = |\zeta_1, \zeta_2, \dots, \zeta_m\rangle = \frac{1}{\sqrt{M!}}\hat{A}\prod_{m=1,M}(a_{1m}|1_m\rangle + a_{0m}|0_m\rangle) =$$

$$= \frac{1}{\sqrt{M!}} det\begin{bmatrix} \zeta_1(1) & \cdots & \zeta_M(1) \\ \vdots & \ddots & \vdots \\ \zeta_1(M) & \cdots & \zeta_M(M) \end{bmatrix} \quad \text{(S2)}$$

Notice that the $M \times M$ matrix in (S2) is of the size of the number of orbitals. It is bigger than the $S \times S$ matrix of the size of the number of electrons, used in standard theory of many-body Fermionic systems[3]. A particular ZS (S2) $|\boldsymbol{\zeta}^{(b)}\rangle$ can be denoted as

$$|\boldsymbol{\zeta}^{(b)}\rangle = \begin{bmatrix} a_{11}^{(b)} & \dots & a_{1M}^{(b)} \\ a_{01}^{(b)} & \dots & a_{0M}^{(b)} \end{bmatrix} \quad \text{(S3)}$$

The first low index in the amplitude $a_{1m}^{(b)}$ or $a_{0m}^{(b)}$ is either 1 or 0 and labels "life" or "death", the index *m* is that of a spin-orbital, and the upper index (*b*) refers to the particular ZS. Then, the overlap of two ZSs is given simply as

$$\Omega_{ab} = \langle \boldsymbol{\zeta}^{(a)} | \boldsymbol{\zeta}^{(b)} \rangle = \prod_{m=1,M} \left(a_{1m}^{(b)*} a_{1m}^{(a)} + a_{0m}^{(b)*} a_{0m}^{(a)} \right) \quad \text{(S4)}$$

A standard Fock Space "physical" electronic structure configuration with *S* electrons occupying *S* out of *M* orbitals are given by ZSs with *S* ones and M-S zeros in the 1st row, meaning *S* fully alive electrons (or S occupied spin-orbitals) and *M-S* fully dead electrons (or unoccupied spin-orbitals):

$$|\boldsymbol{\zeta}^{(110\ldots1)}\rangle = \begin{bmatrix} 110 & \ldots & 1 \\ 001 & \ldots & 0 \end{bmatrix} \quad \text{(S5)}$$

This way of enumerating of the Fock space configurations has been used in the ref [4] where it was shown to have certain bookkeeping advantages. In this paper we go further assuming arbitrary amplitudes of $|1_m\rangle$ and $|0_m\rangle$ states. The space of all 2^M Fock states ranging from zero occupancy $|\boldsymbol{\zeta}^{(000\ldots0)}\rangle$ to full occupancy $|\boldsymbol{\zeta}^{(111\ldots1)}\rangle$ is a Full Fock Space (FFS). A wave function

$$|\Psi\rangle = \sum_{b=1,K} A^{(b)} |\boldsymbol{\zeta}^{(b)}\rangle \quad \text{(S6)}$$

can be manipulated by acting on it with fermionic creation and annihilation operators. A simple sign changing rule has been proposed, which expresses Wigner-Jourdan rule for Zombie States. Acting on the *m*-th spin-orbital also changes sign of the amplitudes of alive electron for *l*<*m*.

$$\hat{a}_{Fm}^{\dagger} |\boldsymbol{\zeta}^{(b)}\rangle = \begin{bmatrix} -a_{11}^{(b)} & -a_{12}^{(b)} & \ldots & -a_{1\,m-1}^{(b)} & a_{0m}^{(b)} & a_{1\,m+1}^{(b)} & \ldots & a_{1M}^{(b)} \\ a_{01}^{(b)} & a_{01}^{(b)} & \ldots & a_{0\,m-1}^{(b)} & 0 & a_{0\,m+1}^{(b)} & \ldots & a_{0M}^{(b)} \end{bmatrix}$$

$$\hat{a}_{Fm} |\boldsymbol{\zeta}^{(b)}\rangle = \begin{bmatrix} -a_{11}^{(b)} & -a_{12}^{(b)} & \ldots & -a_{1\,m-1}^{(b)} & 0 & a_{1\,m+1}^{(b)} & \ldots & a_{1M}^{(b)} \\ a_{01}^{(b)} & a_{01}^{(b)} & \ldots & a_{0\,m-1}^{(b)} & a_{1m}^{(b)} & a_{0\,m+1}^{(b)} & \ldots & a_{0M}^{(b)} \end{bmatrix} \quad \text{(S7)}$$

Changing the sign of the alive amplitudes in the top row for all elements on the left follows from the antisymmetric nature of fermionic wave functions described by anticommuting of fermionic operators[1]. It replaces Jordan-Wigner factor which appears in front of a standard Slater determinant due to permuting a column corresponding to the *m*–th orbital of the usual Slater matrix to the left where it is acted upon with creation or annihilation operators $\hat{a}_{Fm}^{\dagger}$ or $\hat{a}_{Fm}$. See ref[3]

The number of electrons in a Zombie State is not well defined. In general a ZS may include contributions of all possible numbers of electrons from zero to *M* and a wave function expressed as a superposition of Zombie states is not guaranteed to be an eigen state of the number operator. As has been shown in the ref[5] a special procedure called cleaning can be developed, which projects wave functions in the zombie state on the Fock subspace with the right number of electrons and improves greatly the accuracy of the wave functions.

ZS formalism provides easy derivation of the matrix element (16). Matrix element is nonzero only between configurations (11) in the states (a) and (b) which differ only by population of *i* and *j* spin-orbital. In the ZS language the eq (15) becomes:

$$\hat{a}_{Fj}\begin{bmatrix} \dots & \zeta_{m_1}^{(a)} & \dots & 0 & \dots & \zeta_j^{(a)} & \dots \\ \dots & 0 & \dots & 1 & \dots & 0 & \dots \end{bmatrix} = \begin{bmatrix} \dots & -\zeta_{m_1}^{(a)} & \dots & 0 & \dots & 0 & \dots \\ \dots & 0 & \dots & 1 & \dots & \zeta_j^{(a)} & \dots \end{bmatrix} \quad \text{(S8)}$$

where $\begin{bmatrix} \dots \\ 0 \\ 1 \\ \dots \end{bmatrix}$ represents the *i*-th column. Similarly

$$\hat{a}_{Fi}\begin{bmatrix} \dots & \zeta_{m_1}^{(b)} & \dots & \zeta_i^{(b)} & \dots & 0 & \dots \\ \dots & 0 & \dots & 0 & \dots & 1 & \dots \end{bmatrix} = \begin{bmatrix} \dots & -\zeta_{m_1}^{(b)} & \dots & 0 & \dots & 0 & \dots \\ \dots & 0 & \dots & \zeta_i^{(b)} & \dots & 1 & \dots \end{bmatrix} \quad \text{(S9)}$$

where $\begin{bmatrix} \dots \\ 0 \\ 1 \\ \dots \end{bmatrix}$ represents the *j*-th column. Then the origin of the sign changing in the eq (16) and the factor $\xi_i^{(b)*}\xi_j^{(a)}$ there becomes obvious after calculating ZS overlap (S4) between (S8) and (S9).

References

1. Shalashilin, D. V., Zombie states for description of structure and dynamics of multi-electron systems. *Journal of Chemical Physics* **2018,** *148* (19), 194109.
2. Perelomov, A., *Generalized Coherent States and Their Applications*. Springer Berlin Heidelberg: 2012.
3. Szabo, A.; Ostlund, N. S., *Modern Quantum Chemistry: Introduction to Advanced Electronic Structure Theory*. Dover Publications: 1989.
4. Streltsov, A. I.; Alon, O. E.; Cederbaum, L. S., General mapping for bosonic and fermionic operators in Fock space. *Physical Review A* **2010,** *81* (2), 12.
5. Bramley, O. A.; Hele, T. J. H.; Shalashilin, D. V., Electronic energies from coupled fermionic "Zombie" states' imaginary time evolution. *The Journal of Chemical Physics* **2022,** *156* (17), 174116.