Approximating the full configuration interaction (FCI) solution for the many-electron electronic Schrödinger equation accurately, based on a basis set expansion, is still a challenging task in ab initio quantum theory in chemistry and physics especially for strongly correlated electronic systems. One of the most significant advancements in this context is the density matrix renormalization group (DMRG) [1, 2], which has increased the applicability of the FCI wave function approach. The limitation of the basis set convergence has been transcended by the F12 theory for complex systems [3]. Stochastic approaches in configuration space [4–7] have also been increasing the efficacy as a new means to approximate the FCI solution with reduced memory requirements, which has stimulated the investigation of adaptive CI methods as their deterministic alternatives in recent years [8–10]. Nevertheless, such approaches based on a linear expansion presented long ago, e.g. Ref. 11, necessitate a truncation in the configuration space accompanying a size-inconsistency error, which is difficult to prevent completely once initiated from a truncated CI expansion.

Coupled-cluster (CC) theory [12, 13] features the size-extensivity a priori owing to the exponential wave function ansatz, and has been the most successful framework in ab initio quantum chemistry for single-reference molecules. Unfortunately, CC treatments of strongly correlated systems require the inclusion of higher-rank cluster operators within a single-reference framework, and such an implementation permitting very high excitations has been realized so far only with the help of an FCI code [14] or automated code synthesis [15]. Therefore, the development of a CC alternative to the adaptive CI has been quite limited to date. An adaptive coupled-cluster (@CC) approach [16], which utilizes an importance selection function has been proposed and tested with the assistance of code synthesis [17] for systems where FCI calculations are feasible. More recently, cluster decomposition of FCI wave functions has been introduced to investigate cluster operators needed for describing strongly correlated systems [18]. Stochastic adaptations of CC [19], coupled-electron pair approximation (CEPA) [20], and selecting higher-order clusters [21] have also been developed.

In this Letter, a novel approach for the computation of many-fermionic systems is introduced based on the full coupled-cluster (FCC) expansion. Systematic reductions are developed in the necessary projection manifold and commutator operations to exploit the sparsity of the FCC wave function. In this FCC reduction (FCCR), a proper treatment of the so-called exclusion-principle violating (EPV) terms plays an important role to accelerate the convergence towards the exact solution.

What follows is the setup of the FCC expansion: For a given basis set, the exact solution of the N-electronic Schrödinger equation is expressed either by the linear (FCI) or, equivalently, by the exponential (FCC) ansatz,

$$|\Psi\rangle = (1 + \hat{C}_1 + \hat{C}_2 + \hat{C}_3 + \cdots + \hat{C}_N)|0\rangle$$

(1)

$$= \exp(\hat{T}_1 + \hat{T}_2 + \hat{T}_3 + \cdots + \hat{T}_N)|0\rangle,$$

(2)

where, $\hat{C}_k$ and $\hat{T}_k$ denote $k$-fold excitation operators with respect to a suitable Fermi vacuum $|0\rangle$ of a single Slater-determinant. The dimension of the FCI expansion [11] increases combinatorially with respect to the numbers of electrons and orbitals, while the exponential ansatz [4] is expected to be a much more compact representation with increasing the system-size, as indicated by the formal relation,

$$\hat{T} = \ln(1 + \hat{C})$$

$$= \hat{C} - \hat{C}^2/2 + \hat{C}^3/3 - \hat{C}^4/4 + \cdots,$$

(3)

in which $\hat{T}$ is exempted from disconnected products for separable correlation events in the FCI expansion. This compactification was investigated numerically in the cluster decomposition of FCI wave functions [18].
The standard CC formulae for FCC are used, obtained by the projection of the similarity-transformation of the Schrödinger equation onto the projection manifold of the FCI space \( \{ \langle \kappa | \rangle \} \),
\[
\langle \kappa | \exp(-\hat{T}) \hat{H} \exp(\hat{T}) | 0 \rangle = \langle \kappa | \hat{H} | 0 \rangle + \sum_{\lambda} \langle \kappa | [\hat{H}, \hat{T}_\lambda] | 0 \rangle + \frac{1}{2} \sum_{\lambda \mu} \langle \kappa | [\hat{H}, \hat{T}_\lambda], \hat{T}_\mu] | 0 \rangle + \frac{1}{6} \sum_{\lambda \mu \nu} \langle \kappa | [\hat{H}, \hat{T}_\lambda], \hat{T}_\mu], \hat{T}_\nu] | 0 \rangle + \frac{1}{24} \sum_{\lambda \mu \nu \rho} \langle \kappa | [\hat{H}, \hat{T}_\lambda], \hat{T}_\mu], \hat{T}_\nu], \hat{T}_\rho] | 0 \rangle = 0, \tag{4}
\]
and the state energy,
\[
E = \langle 0 | \hat{H} \exp(\hat{T}) | 0 \rangle,
\tag{5}
\]
where the cluster operator is
\[
\hat{T} = \sum_{\lambda} \hat{T}_\lambda = \sum_{\lambda} t_\lambda \hat{a}_\lambda,
\tag{6}
\]

\( \kappa, \lambda, \ldots \) stand for sets of particle-hole excitation indices, and \( t_\lambda \) and \( \hat{a}_\lambda \) are cluster amplitudes and the corresponding excitation operators, \( |\lambda\rangle = \hat{a}_\lambda | 0 \rangle \), respectively.

The present implementation of FCC employs a direct binary representation of \( \hat{a}_\lambda \) for the occupations of the \( \alpha \) and \( \beta \) strings of the resulting Slater-determinants \( |\lambda\rangle \) subject to the normalization \( \langle \kappa | \lambda \rangle = \delta_{\kappa \lambda} \). The commutators through the quartic order in \( \hat{T} \) are computed explicitly for a given set of arguments \( \{ \kappa, \lambda, \mu, \ldots \} \) corresponding to the projection \( \langle \kappa | \rangle \) and excitations \( \hat{a}_\lambda, \hat{a}_\mu, \ldots \) by expanding the commutators into a sum of Hamiltonian matrix elements over Slater-determinants. For instance, the expansion
\[
\langle \kappa | [\hat{H}, \hat{a}_\lambda], \hat{a}_\mu], \hat{a}_\nu] | 0 \rangle = \langle \kappa | \hat{H} \hat{a}_\lambda \hat{a}_\mu \hat{a}_\nu | 0 \rangle - \langle \kappa | \hat{a}_\lambda \hat{H} \hat{a}_\mu \hat{a}_\nu | 0 \rangle - \langle \kappa | \hat{a}_\lambda \hat{a}_\mu \hat{H} \hat{a}_\nu | 0 \rangle - \langle \kappa | \hat{a}_\lambda \hat{a}_\mu \hat{a}_\nu \hat{H} | 0 \rangle + \langle \kappa | \hat{a}_\lambda \hat{a}_\mu \hat{a}_\nu \hat{H} | \lambda \rangle - \langle \kappa | \hat{a}_\lambda \hat{a}_\mu \hat{a}_\nu \hat{H} | 0 \rangle, \tag{7}
\]
is performed inside a naive 4-fold loop over \( \lambda, \mu, \nu, \) and \( \kappa \), and the actions of the excitation and de-excitation operators, \( \hat{a}_\mu | \nu \rangle, \hat{a}_\lambda | \mu \rangle, \hat{a}_\lambda \hat{a}_\mu | \nu \rangle, \hat{a}_\lambda^\dagger | \kappa \rangle, \hat{a}_\mu^\dagger | \kappa \rangle, \hat{a}_\mu^\dagger \hat{a}_\lambda^\dagger | \kappa \rangle, \hat{a}_\mu^\dagger \hat{a}_\mu^\dagger | \kappa \rangle, \hat{a}_\mu^\dagger \hat{a}_\lambda^\dagger \hat{a}_\mu^\dagger | \kappa \rangle, \) are converted to signed Slater-determinants. Then, the Hamiltonian matrix elements over the determinants are assembled for \( \hat{T} \). The loop over the projection \( \langle \kappa | \rangle \) is not a mandatory setup within FCC since only a limited number of \( \langle \kappa | \rangle \) interact with the contractions of \( [\hat{H}, \hat{a}_\lambda], \hat{a}_\mu], \hat{a}_\nu] | 0 \rangle \). Nevertheless, this structure is retained keeping the capability of cluster operator selections in mind. Alternatively, several criteria to rapidly discriminate between a combination of the arguments \( \{ \kappa, \lambda, \mu, \ldots \} \) giving a null result are introduced in a highly parallelizable manner.

The above process is carried out using a numerical library for quantum Monte Carlo calculations in configuration space \( \mathcal{N} \) containing bitwise operations over Slater-determinants in the binary representations. It is also stressed that the present FCC implementation is suitable for introducing screenings exploiting the sparsity of the exponential ansatz compared to the previous higher-order CC using intermediates.

The FCCCR approach is detailed below: The first-order interacting space of the Fermi vacuum spans the singles and doubles (SD) for the CCSD model. Then, only the one-rank higher excitation manifold \( \langle \kappa | \rangle \) in the space generated by the CCSD is incorporated by taking the single commutator \( [\hat{H}, \hat{T}] \) using \( \hat{T} \) converged in the proceeding CC calculation. This update is successively continued until the entire Hilbert space for FCC is integrated. In this case, the great majority of cluster operators \( \hat{T}_\lambda \) in FCC would possess nearly-null amplitudes unlike those in FCI. Accordingly, the corresponding excitations connected to these operators are unwanted from the projection manifold. A necessary modification to this update in FIG. 11 from this sparsity is to expand the excitation manifold using the primary set of cluster operators with absolute amplitudes exceeding the connectivity screening threshold, \( \vartheta_C \), as
\[
\hat{T}_\kappa \leftrightarrow \langle \kappa | [\hat{H}, \hat{T}_\lambda] | 0 \rangle \quad \forall |t_\lambda| > \vartheta_C. \tag{8}
\]
The excitation manifold of FCCR is formed as a subspace of the FCC model discarding the space connected with nearly-null clusters, and FCCR reduces to FCC in the limit, \( \vartheta_C = 0 \). The connectivity through the higher-order commutators is suitably incorporated by iteratively updating the excitation manifold applying the single commutators. Incidentally, it turned out that the use of the single commutator for the same purpose was independently conceived by Evangelista \( \text{[23]} \).

For cluster operators in the space generated by the
method described above, the attenuation in the amplitude of the disconnected products further allows us to reduce the operations of the commutators in Eq. 4. Due to the nonlinear nature of the exponential commutator contributions to (9) are negligible even after the formation of the FCCR excitation manifold. Accordingly, the working equation is modified as
\[
\langle \kappa | e^{-T_h} e^{T} | 0 \rangle = \langle \kappa | \hat{H}_\kappa | 0 \rangle + \sum_{\lambda \neq \kappa} \langle \kappa | [\hat{H}_\kappa, T_\lambda] | 0 \rangle + \frac{1}{2} \sum_{(\lambda \mu \neq \kappa)} \langle \kappa | [\hat{H}_\kappa, T_\lambda, T_\mu] | 0 \rangle + \frac{1}{6} \sum_{(\lambda \mu \nu \neq \kappa)} \langle \kappa | [\hat{H}_\kappa, T_\lambda, T_\mu, T_\nu] | 0 \rangle + \frac{1}{24} \sum_{(\lambda \mu \nu \omega \neq \kappa)} \langle \kappa | [\hat{H}_\kappa, T_\lambda, T_\mu, T_\nu, T_\omega] | 0 \rangle = 0, \tag{9}
\]
such that the commutators with small amplitudes are discarded using the operation screening threshold \( \vartheta_O \), where it is defined that \( \hat{H}_\kappa = \exp(-T_\kappa) \hat{H} \exp(T_\kappa) \), whose triple and quadruple commutator contributions to (9) are null due to the coincident excitation indices, and the limitation in the summation, \( \ldots \neq \kappa \), means none of the indices in parentheses takes the value of \( \kappa \). Eq. (9) becomes exact in the limit \( \vartheta_O \to 0 \). Importantly, most of the terms with finite power in \( T_\kappa \) are EPV, and the summation is preserved irrespective of the amplitude \( t_\kappa \). This EPV form of the working equation is significant in improving the convergence with respect to \( \vartheta_O \) compared to the expansion in the non-EPV form, i.e. the summation is performed for e.g. \( |t_\kappa t_\omega| > \vartheta_O \).

The efficiency of the FCCR approach is now examined using small molecules in which both dynamic and non-dynamic correlation effects are important. The excitation manifold is generated iteratively using \( \vartheta_O = \min(4 \times 10^{-4}, \vartheta_C) \) for a given connectivity screening threshold \( \vartheta_C \) until the subsequent CC energy difference becomes less than 0.1mE\(_{\text{h}}\) for the duration of this study, and then \( \vartheta_O \) is reduced for the refinement of the energy. FIG. 2 shows the convergence of the FCCR correlation energies for stretched \( \mathrm{N}_2 \) by changing \( \vartheta_C \) and \( \vartheta_O \) around the most difficult bond distance. The number of induced cluster amplitudes increases from \( 2.2 \times 10^6 \) to \( 6.4 \times 10^8 \) with tightening \( \vartheta_C \) in the update in the EPV form. With respect to \( \vartheta_O \), the FCCR energies tend to converge from below when the EPV form is not applied. This can be attributed to surplus screening in the quadratic terms compared to the single commutators. Amongst the quadratic terms, the contribution of EPV is usually quite large as known in CEPA [23], and the EPV form indeed ameliorates the situation satisfactorily exhibiting almost variational convergence.

The next example is the singlet-triplet splitting of acenes. FIG. 3 shows the growth in the numbers of the generated total and primary amplitudes, \( N_T \) and \( N_P \), with increasing the number of fused benzene rings. The increase in \( N_T \) is much milder than in the FCI dimension, e.g. the numbers of the generated FCCR amplitude is 6 order of magnitude smaller than the FCI dimension for hexacene both for the singlet and triplet states. The lines for \( N_P \) over the number of rings (in yellow) are almost flat beyond anthracene, indicating that the pri-
TABLE I. The deviations of the FCCR singlet and triplet energies \((mE_h)\) with respect to DMRG \([22]\), \(\Delta E_{\text{FCCR}} = E_{\text{FCCR}} - E_{\text{DMRG}}\), and the arising splittings \(\Delta ST\) (kcal/mol) for the model acenes. The operation thresholds are defined as \(\vartheta_O^{\text{Loose}} = 3 \times 10^{-4}\), \(\vartheta_O^{\text{Middle}} = 3 \times 10^{-5}\), and \(\vartheta_O^{\text{Tight}} = 3 \times 10^{-6}\).

|          | \(\Delta E_{\text{FCCR}}\) (Singlet) | \(\Delta E_{\text{FCCR}}\) (Triplet) | \(\Delta ST\) (FCCR) | \(\Delta ST\) (DMRG) |
|----------|---------------------------------|---------------------------------|----------------|----------------|
|          | \(\vartheta_O^{\text{Loose}}\) | \(\vartheta_O^{\text{Middle}}\) | \(\vartheta_O^{\text{Tight}}\) | \(\vartheta_O^{\text{Loose}}\) | \(\vartheta_O^{\text{Middle}}\) | \(\vartheta_O^{\text{Tight}}\) |
| naphtalene | 0.3 | 0.0 | 0.1 | 2.0 | 0.0 | 0.0 | 61.5 | 61.5 | 61.5 | 61.5 |
| anthracene | 2.1 | 0.1 | 0.1 | 2.1 | 0.1 | 0.0 | 45.9 | 46.0 | 45.9 | 45.9 |
| tetracene | 7.6 | 0.4 | 0.1 | 7.2 | 0.7 | 0.2 | 34.6 | 35.0 | 34.8 | 34.7 |
| pentacene | 16.4 | 0.9 | 0.1 | 16.1 | 1.8 | 0.4 | 26.4 | 27.3 | 26.9 | 26.7 |
| hexacene | 26.7 | 1.8 | 0.0 | 26.9 | 3.2 | 0.5 | 21.1 | 21.9 | 21.3 | 21.0 |

TABLE II. The number of primary and total amplitudes, \(N_P\) and \(N_T\), respectively, and the state energy of FCCCR for \(\text{C}_2\) in \(E_h\) compared to truncated CC and DMRG \([27]\) correlating 24 electrons in 30 RHF orbitals of the SV basis set of Ahlrichs \([27]\) with different connectivity thresholds. The tighter operation screening threshold, \(\vartheta_O = 3 \times 10^{-7}\), is employed for this system, which shows slow and non-variational convergence with respect to \(\vartheta_O\).

|          | \(\vartheta_O\) | \(N_P\) (M) | \(N_T\) | \(E\) |
|----------|----------------|------------|--------|------|
| FCCCR    | 6.0 \times 10^{-7} | 11,399 | 8,909,199 | -2086.4159 |
|          | 4.0 \times 10^{-4} | 19,244 | 15,162,543 | -2086.4169 |
|          | 2.0 \times 10^{-4} | 42,813 | 32,043,659 | -2086.4186 |
|          | 1.0 \times 10^{-4} | 95,849 | 68,766,328 | -2086.4203 |
| CCSD     | 8,766 | -2086.3225 |
| CCSDT    | 598,082 | -2086.3805 |
| CCSDTQP  | 23,422,496 | -2086.4067 |
| DMRG     | 560,106,440 | -2086.4144 |
| Extrapolated | \infty | -2086.4210 |

\(a\) The number of renormalized states \(M\) for DMRG.

Finally, the convergence of the total energy of \(\text{C}_2\) at a bond length of 1.5 Å is shown in Table III. This system is very slow in the convergence of excitation ranks, and non-negligible septime and octuple excitations appear in accordance with the observations of Lehtola et al. \([18]\). The energies of the truncated CC are higher than those of FCCCR even for the CCSDTQ model with 560 million amplitudes due to the absence of these high-rank cluster operators. With tightening \(\vartheta_C\), the FCCCR energy decreases, and the case employing 69 million amplitudes gives -2086.4203 \(E_h\), that is only 0.7 \(mE_h\) higher than the best extrapolated DMRG estimate of -2086.4210 \(E_h\) \([26]\).

In conclusion, FCCCR has been introduced based on an FCC of direct commutator expansions. The sparsity of the cluster operators facilitates efficient screenings for the excitation manifold and commutator operators. Although high-rank cluster operators are needed for strong electron correlation, the treatment is feasible provided the amplitudes are not prohibitively numerous. Therefore, FCCCR appears to be a promising means for strongly correlated electronic systems in a balanced descriptions of dynamic and non-dynamic correlation effects. Note that FCCCR can also be implemented in terms of the Wick theorem instead of the direct commutator expansions, e.g., (i) acceleration of convergence using a different choice of Fermi vacuum including Bruecknerization, (ii) orbital rotations in the occupied and virtual spaces, (iii) perturbative corrections with respect to the complementary space connected to the secondary cluster operators, and so on. This line of research, with applications including more challenging systems, will be pursued and reported in the near future.

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[1] S. R. White, Phys. Rev. Lett. 69, 2863 (1992).
[2] G. K.-L. Chan and S. Sharma, Annu. Rev. Phys. Chem. 62, 465 (2011).
[3] A. Grüneis, S. Hirata, Y.-y. Ohnishi, and S. Ten-no, J. Chem. Phys. 146, 080901 (2017).
[4] G. H. Booth, A. J. W. Thom, and A. Alavi, J. Chem. Phys. 131, 054106 (2009).
[5] D. Ciepland, G. H. Booth, and A. Alavi, J. Chem. Phys. 132, 174104 (2010).
[6] F. R. Petruzielo, A. A. Holmes, H. J. Changlani, M. P. Nightingale, and C. J. Umrigar, Phys. Rev. Lett. 109, 230201 (2012).
[7] S. Ten-no, J. Chem. Phys. 138, 164126 (2013).
[8] J. B. Schriber and F. A. Evangelista, J. Chem. Phys. 144, 161106 (2016).
[9] N. M. Tubman, J. Lee, T. Y. Takeshita, M. Head-Gordon, and K. B. Whaley, J. Chem. Phys. 145, 044112 (2016).
[10] A. A. Holmes, N. M. Tubman, and C. J. Umrigar, J. Chem. Theory Comput. 12, 3674 (2016).
[11] B. Huron, J. P. Malrieu, and P. Rancurel, J. Chem. Phys. 58, 5745 (1973).
[12] J. Čiček, J. Chem. Phys. 45, 4256 (1966).
[13] R. J. Bartlett and M. Musial, Rev. Mod. Phys. 79, 291 (2007).
[14] S. Hirata and R. J. Bartlett, Chem. Phys. Lett. 321, 216 (2000).
[15] M. Kállay and P. R. Surján, J. Chem. Phys. 115, 2945 (2001).
[16] D. I. Lyakh and R. J. Bartlett, J. Chem. Phys. 133, 244112 (2010).
[17] D. I. Lyakh, private communication (2018).
[18] S. Lehtola, N. M. Tubman, K. B. Whaley, and M. Head-Gordon, J. Chem. Phys. 147, 154105 (2017).
[19] A. J. W. Thom, Phys. Rev. Lett. 105, 263004 (2010).
[20] S. L. Ten-no, J. Chem. Phys. 147, 244107 (2017).
[21] J. E. Deustua, J. Shen, and P. Piecuch, Phys. Rev. Lett. 119, 223003 (2017).
[22] F. A. Evangelista, private communication (2018).
[23] S. Koch and W. Kutzelnigg, Theoret. Chim. Acta 59, 387 (1981).
[24] J. Hachmann, J. J. Dorando, M. Avilés, and G. K.-L. Chan, J. Chem. Phys. 127, 134309 (2007).
[25] Supplementary material.
[26] S. Sharma and G. K.-L. Chan, J. Chem. Phys. 136, 124121 (2012).
[27] A. Schäfer, H. Horn, and R. Ahlrichs, J. Chem. Phys. 97, 2571 (1992).
[28] R. Bartlett and M. Musial, J. Chem. Phys. 125, 204105 (2006).