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We propose a new approach to the determination of accurate electronic energies that are equivalent to the results of high-level coupled-cluster (CC) calculations. The approach is based on merging the CC(P;Q) formalism, which corrects energies obtained with an arbitrary truncation in the cluster operator, with the stochastic configuration interaction and CC ideas. The advantages of the proposed methodology are illustrated by molecular examples, where the goal is to recover the energetics obtained in the CC calculations with a full treatment of singly, doubly, and triply excited clusters.

One of the goals of electronic structure theory is to precisely describe increasingly complex polyatomic systems. It is generally accepted that size extensive methods based on the exponential wave function ansatz [1, 2] of coupled-cluster (CC) theory [3–7], $|\Psi\rangle = e^T|\Phi\rangle$, where $T = \sum_{n=1}^{N} T_n$ is the cluster operator, with T_n representing its n-particle–n-hole (npnh) component and N the number of correlated electrons, and $|\Phi\rangle$ is the reference determinant defining the Fermi vacuum, are excellent candidates for addressing this goal. Indeed, when applied to molecular properties and chemical reaction pathways, the CC hierarchy, including CCSD, where T is truncated at T_2 [8, 9], CCSDT, where T is truncated at T_3 [10, 11], CCSDTQ, where T is truncated at T_4 [12, 13], etc., rapidly converges to the limit of the exact, full configuration interaction (FCI) diagonalization of the Hamiltonian [14] (we adopt commonly accepted quantum chemistry acronyms, where S, D, T, and Q stand for single (1p1h), double (2p2h), triple (3p3h), and quadruple (4p4h) excitations). One of the key challenges is to incorporate T_n components with $n > 2$, needed to achieve a quantitative description, without running into prohibitive computational costs of CCSDT and similar schemes, while eliminating failures of the more practical perturbative approximations of the CCSD(T) [15] type in multi-reference situations, such as bond breaking [14, 16, 17]. A similar challenge applies to other areas of many-body theory, such as nuclear physics, where CC methods enjoy renaissance [18–20].

In this letter, we propose a new way of obtaining accurate energetics equivalent to high-level CC calculations, even when electronic quasi-degeneracies and higher–than–two-body clusters become significant, at the small fraction of the computational cost, while preserving the black-box character (minimum input information) of conventional single-reference computations. The key idea is a merger of the deterministic methodology, abbreviated as CC(P;Q) [21–24], with the stochastic FCI Quantum Monte Carlo (FCIQMC) [25, 26] and CC Monte Carlo (CCMC) [27–30] approaches. As shown in Figs. 1–3 and the Supplemental Material [31], where one aims at recovering the CCSDT results, the stochastic CC(P;Q) calculations, using FCIQMC or CCMC to identify the leading determinants or cluster amplitudes in the wave function and the *a posteriori* CC(P;Q) corrections to capture the remaining correlations, rapidly converge to the target energetics based on the information extracted from the early stages of FCIQMC or CCMC propagations.

We begin by summarizing the most essential ingredients of CC(P;Q), FCIQMC, and CCMC methodologies. In the CC(P;Q) formalism, the ground-state energy of a N-electron system is determined in two steps. In the first step, abbreviated as CC(P), we solve the CC equations in the subspace of the N-electron Hilbert space $\mathscr{H}$, designated as $\mathscr{H}^{(P)}$ and referred to as the P space, which is spanned by the excited determinants $|\Phi_K\rangle = E_K|\Phi\rangle$ that together with the reference determinant $|\Phi\rangle$ dominate the wave function $|\Psi\rangle$ of interest (E_K is the elementary particle-hole excitation operator generating $|\Phi_K\rangle$ from $|\Phi\rangle$). This means that we approximate the cluster operator T by $T^{(P)} = \sum_{|\Phi_K\rangle \in \mathscr{H}^{(P)}} t_K E_K$ and determine the cluster amplitudes t_K by solving the system $\mathfrak{M}_K(P) = 0$, $|\Phi_K\rangle \in \mathscr{H}^{(P)}$, obtained by projecting the Schrödinger equation for the CC wave function with $T = T^{(P)}$ on $\mathscr{H}^{(P)}$ [14]. Here, $\mathfrak{M}_K(P) = \langle\Phi_K|\bar{H}^{(P)}|\Phi\rangle$ where $\bar{H}^{(P)} = e^{-T^{(P)}} H e^{T^{(P)}}$, are moments of the P-space CC equations [32]. Once $T^{(P)}$ and the corresponding ground-state energy $E^{(P)} = \langle\Phi|\bar{H}^{(P)}|\Phi\rangle$ are determined, we calculate the non-iterative correction [21, 22]

$$\delta(P;Q) = \sum_{|\Phi_K\rangle \in \mathscr{H}^{(Q)}} \ell_K(P)\,\mathfrak{M}_K(P) \qquad (1)$$

to $E^{(P)}$, which accounts for the many-electron correlation effects captured by the second subspace of $\mathscr{H}$, referred to as the Q space and designated as $\mathscr{H}^{(Q)}$ ($\mathscr{H}^{(Q)} \subseteq (\mathscr{H}^{(0)} \oplus \mathscr{H}^{(P)})^\perp$, where $\mathscr{H}^{(0)}$ is a one-dimensional subspace spanned by $|\Phi\rangle$). The $\ell_K(P)$ coefficients are defined as $\ell_K(P) = \langle\Phi|(1 + \Lambda^{(P)})\bar{H}^{(P)}|\Phi_K\rangle/D_K(P)$, where

$\Lambda^{(P)} = \sum_{|\Phi_K\rangle \in \mathscr{H}^{(P)}} \lambda_K (E_K)^\dagger$ is the hole-particle deexcitation operator that generates the bra state $\langle \tilde{\Psi}^{(P)} | = \langle \Phi | (1 + \Lambda^{(P)}) e^{-T^{(P)}}$ matching the CC(P) ket state $|\Psi^{(P)}\rangle = e^{T^{(P)}} |\Phi\rangle$ and $D_K(P) = E^{(P)} - \langle \Phi_K | \bar{H}^{(P)} | \Phi_K \rangle$. The final CC($P$;$Q$) energy is calculated as

$$E^{(P+Q)} = E^{(P)} + \delta(P;Q). \quad (2)$$

We distinguish between full CC(P;Q) using the Epstein–Nesbet denominator $D_K(P)$ entering the $\ell_K(P)$ amplitudes, as described above, abbreviated as CC(P;Q)$_{\text{EN}}$, and the CC(P;Q)$_{\text{MP}}$ framework using the Møller–Plesset form of $D_K(P)$ [23].

The CC(P;Q) formalism can be used in several ways. For example, if $\mathscr{H}^{(P)}$ is spanned by all $|\Phi_{i_1 \ldots i_n}^{a_1 \ldots a_n}\rangle$ determinants with the excitation rank $n \leq L$, where $i_1, i_2, \ldots$ ($a_1, a_2, \ldots$) are the spin-orbitals occupied (unoccupied) in $|\Phi\rangle$, and $\mathscr{H}^{(Q)}$ by those with $L < n \leq M$, where $M \leq N$, one obtains the completely renormalized CC hierarchy [21, 33, 34]. The resulting and related [16, 32, 35–37] approaches improve poor performance of CCSD(T) in bond breaking situations, but like CCSD(T) they decouple the higher-order T_n components, such as T_3 or T_3 and T_4, from their lower-order T_1 and T_2 counterparts. There are important problems, such as the automerization of cyclobutadiene discussed later, where this can be detrimental to the resulting potential energy surfaces and activation energies [21–24]. One can address this concern by including selected triply or triply and quadruply excited determinants, in addition to all singles and doubles, in the P space, as in the active-space considerations [17], while using corrections $\delta(P;Q)$ to account for the remaining T_3 or T_3 and T_4 cluster amplitudes [21–24], but this requires the *a priori* knowledge of the dominant 3p3h or 3p3h and 4p4h excited determinants for the inclusion in the P space, which are system dependent and subjectively chosen by the user. *Questions arise if there is an automated way of determining P spaces reflecting on the nature of states being calculated, while using corrections $\delta(P;Q)$ to capture the remaining correlations of interest, and if this can be done such that the resulting electronic energies rapidly converge to their high-level (e.g., CCSDT) parents, even when higher–than–two-body clusters become large, at the small fraction of the computational effort and with an ease of a black-box computation.*

This letter shows that both questions have positive answers if we fuse the deterministic CC(P;Q) methodology with the stochastic FCIQMC and CCMC ideas. The main idea of FCIQMC, originally introduced in [25], is that of a stochastic population dynamics of a set of walkers, which simulates the underlying imaginary-time Schrödinger equation in the many-fermion Hilbert space spanned by Slater determinants. The walkers, which can carry positive or negative signs, inhabit the Slater determinant space and evolve according to simple rules that include spawning, birth or death, and annihilation. Once
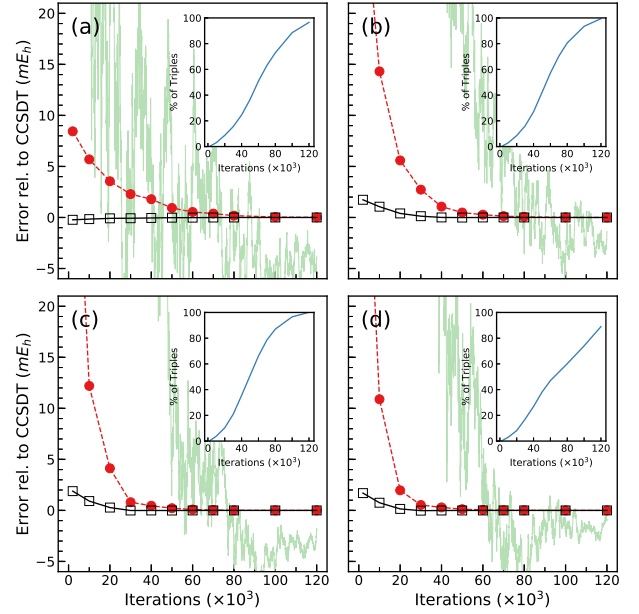

FIG. 1. Convergence of the CC(P) (red filled circles and dashed lines) and CC(P;Q)$_{\text{EN}}$ (black open squares and solid lines) energies toward CCSDT for the F_2/cc-pVDZ molecule in which the F–F distance R was set at (a) R_e, (b) $1.5R_e$, (c) $2R_e$, and (d) $5R_e$, where $R_e = 2.66816$ bohr is the equilibrium geometry. The P spaces consisted of all singles and doubles and subsets of triples identified during the i-FCIQMC propagations with $\delta\tau = 0.0001$ a.u. (depicted by the green lines representing the corresponding projected energies). The Q spaces consisted of the triples not captured by i-FCIQMC. All energies are errors relative to CCSDT in millihartree and the insets show the percentages of triples captured during the i-FCIQMC propagations.
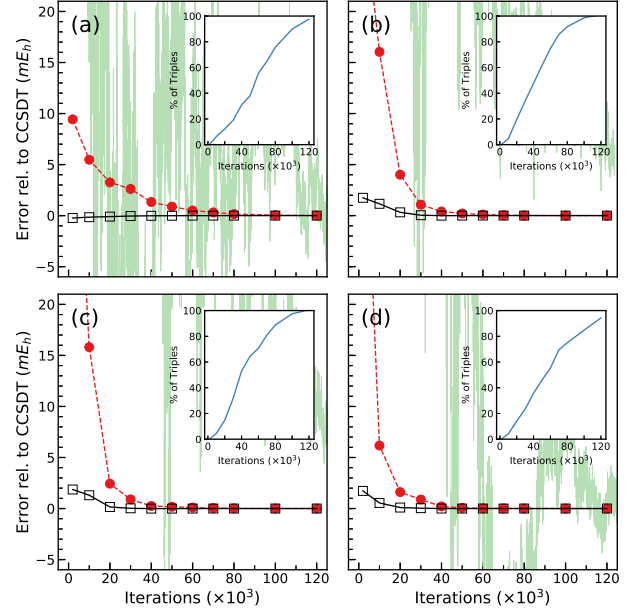

FIG. 2. Same as Fig. 1 except that the subsets of triples included in the CC(P) calculations are now identified by the i-CCSDT-MC simulations and the corresponding Q spaces consist of the triples not captured by i-CCSDT-MC.

a critical number of walkers is reached, one begins to stabilize their population using suitable energy shifts. Upon convergence, the FCIQMC propagation produces a FCI-level state and energy without any *a priori* knowledge of the nodal structure of the wave function needed in traditional QMC. Several ideas have been explored to improve the original FCIQMC scheme and accelerate its convergence [26, 38–41], including the initiator FCIQMC (*i*-FCIQMC) approach, where only those determinants that acquire walker population exceeding a preset value (n_a) are allowed to spawn new walkers onto empty determinants [26]. FCIQMC can be extended to truncated CI and other many-body schemes [27, 42], including high-level CC theories, resulting in the corresponding CCMC (CCSDT-MC, etc.) methodologies, in which one samples the space of excitation amplitudes (amplitudes of "excitors") by "excips," whose population dynamics converges to the desired CC solution [27–30]. As in FCIQMC, one can use the initiator CCMC (*i*-CCMC) algorithm [29].

The FCIQMC and CCMC methodologies are useful to us, since one can start the corresponding propagations by placing a certain, sufficiently large, number of walkers on a single determinant, which in this letter is the restricted Hartree-Fock (RHF) state, and let the FCIQMC walker or CCMC excip population dynamics capture other determinants, including those that correspond to higher–than–double excitations needed to set up meaningful P spaces in CC(P;Q) considerations. Although one may need longer propagation times τ to stabilize walker (FCIQMC) or excip (CCMC) populations to achieve the desired wave function and energy convergence using purely stochastic means, the most important determinants or cluster amplitude types, which significantly contribute to the wave function in the end, are captured in the early propagation stages, which require small computational effort relative to the target CC calculation. This is illustrated in Figs. 1 and 2 using the challenging F_2 molecule, as described by the cc-pVDZ basis set [43], as an example [33, 34, 44]. We stretch the F–F bond length R from the equilibrium geometry $R_e = 2.66816$ bohr, where the electronic wave function is dominated by large dynamic correlations and where T_3 effects, measured as the difference of the CCSDT and CCSD energies, amount to 9.485 millihartree, to $5R_e$, where F_2 is essentially dissociated and characterized by large non-dynamic correlations, and where T_3 effects of 49.816 millihartree exceed the depth of the CCSDT potential well (the difference between the CCSDT energies at $R = 5R_e$ and $R = R_e$ is 44.210 millihartree; see [33, 34, 44] and the Supplemental Material [31]). Using a time step $\delta\tau = 0.0001$ a.u. and $n_a = 3$, and placing 100 walkers/excips on the RHF determinant to initiate the MC propagations, the green curves "behind" the CC(P) and CC(P;Q) results, which represent the appropriately projected *i*-FCIQMC (Fig. 1) and *i*-CCSDT-MC (Fig. 2) energies, remain quite noisy up to about

100,000 of such time steps (called iterations), suggesting that the walker populations at various determinants and the excip populations corresponding to cluster amplitudes still significantly fluctuate (we used HANDE code [45] to perform the *i*-FCIQMC and *i*-CCSDT-MC computations). At the same time, the CC(P) calculations using $T^{(P)} = T_1 + T_2 + T_3^{(\mathrm{MC})}$, i.e., the CCSDT-type calculations with all singles, represented by T_1, all doubles, represented by T_2, and subsets of triples identified during the *i*-FCIQMC and *i*-CCSDT-MC propagations (triples having at least one positive or negative walker/excip on them), represented by $T_3^{(\mathrm{MC})}$, stabilize rather quickly, reaching sub-millihartree accuracy levels relative to the deterministic CCSDT calculations in 30,000–50,000 iterations (see Table I in the Supplemental Material [31]; all deterministic CC runs used our codes). This suggests that one should be able to rely on the early stages of *i*-FCIQMC or *i*-CCMC propagations to create lists of determinants defining P spaces for CC(P) calculations and then use the CC(P;Q) correction $\delta(P;Q)$ to capture the remaining correlation effects missing in the P-space CC calculations. If our goal is to reproduce the CCSDT energetics, we solve the CC(P) equations with $T^{(P)} = T_1 + T_2 + T_3^{(\mathrm{MC})}$, as described above, and then use $\delta(P;Q)$ to correct the resulting P-space energy $E^{(P)}$ for the remaining triples that were not captured by *i*-FCIQMC or *i*-CCSDT-MC at the time the list of P-space excitations was created. If our target is CCSDTQ, we solve the CC(P) equations with $T^{(P)} = T_1 + T_2 + T_3^{(\mathrm{MC})} + T_4^{(\mathrm{MC})}$ and correct the resulting P-space energy $E^{(P)}$ for the triples and quadruples not captured by *i*-FCIQMC or *i*-CCSDTQ-MC. One can extend this recipe to higher-order CC methods with T_5, T_6, etc. Assuming that the $E^{(P+Q)}$ energies based on the lists of P-space excitations extracted from the early stages of *i*-FCIQMC or *i*-CCMC propagations rapidly converge with τ, we can significantly reduce the computational time of the CCSDT, CCSDTQ, etc. calculations, while practically avoiding the numerical noise associated with the varying walker/excip populations. The CPU time reduction originates from three factors. First, the CPU times associated with the early stages of *i*-FCIQMC or *i*-CCMC dynamics are very short compared to the converged propagations. Second, CC(P) calculations offer significant speedups compared to their parent approaches, when small fractions of triples, triples and quadruples, etc. are involved. For example, if the total number of triples is D and the number of triples in the stochastically determined P space is d, the speedup relative to full CCSDT offered by CC(P) using $T^{(P)} = T_1 + T_2 + T_3^{(\mathrm{MC})}$, when the most expensive $\langle\Phi_{ijk}^{abc}|[H, T_3]|\Phi\rangle$ term in the CCSDT equations is examined, is $(d/D)^2$. Third, the computational cost of determining the CC(P;Q) correction is less than the cost of a single iteration of the target CC calculation. For example, the CPU time required to deter-

mine the $\delta(P;Q)$ correction due to the remaining triples outside the stochastically determined P space scales no worse than $\sim 2n_o^3 n_u^4$, where n_o (n_u) is the number of orbitals occupied (unoccupied) in $|\Phi\rangle$. This should be compared to the $n_o^3 n_u^5$ scaling of each iteration of the target CCSDT calculation, and one typically needs 20–40 iterations to converge to a microhartree level.

All of the above is observed in our numerical tests aimed at recovering full CCSDT energetics. We discuss two molecular examples, where CCSDT is an adequate theory level to obtain highly accurate information [21, 22, 33, 34, 44], namely, the F–F bond dissociation in F_2, summarized in Figs. 1 and 2 and the Supplemental Material [31], and the automerization of cyclobutadiene, using the cc-pVDZ basis set in both cases. We also show the results for F_2 using the larger cc-pVTZ [43] and aug-cc-pVTZ [46] bases (see Fig. 3 and the Supplemental Material [31]). As already explained, the CC(P) calculations with singles, doubles, and subsets of triples extracted during i-FCIQMC and i-CCSDT-MC runs smoothly converge to CCSDT, but the convergence is not as fast as desired. The situation changes when the CC(P) results are corrected for the triples outside the P spaces generated with i-FCIQMC and i-CCSDT-MC. In the case of the F_2/cc-pVDZ molecule, even when $R = 2R_e$ or $5R_e$, where T_3 effects are 45.638 and 49.816 millihartree, respectively, exceeding the dissociation energy, the CC(P;Q) correction, especially CC(P;Q)$_{\text{EN}}$, achieves remarkable, 0.1–0.3 millihartree accuracies relative to CCSDT with only 8–10 % (i-FCIQMC) or 12–20 % (i-CCSDT-MC) of triples in the P space, or after about 20,000 i-FCIQMC or i-CCSDT-MC $\delta\tau = 0.0001$ a.u. iterations, reached in 8–10 wall time seconds on a quad-core Dell Precision T-1700 workstation used in our calculations. The total times (including MC, CC(P), and $\delta(P;Q)$ steps) required by the i-FCIQMC-based CC(P;Q) calculations giving these high accuracy levels vary between 13 seconds at $R = R_e$ and 15 seconds in the $R = 2R_e - 5R_e$ region, with the i-CCSDT-MC-based calculations being similarly inexpensive. With 30,000 MC iterations, which capture 15–21 % of triples in the i-FCIQMC case and 19–34 % of triples in the case of i-CCSDT-MC, we need $\sim 30 - 40$ seconds to complete the CC(P;Q) calculations, recovering the CCSDT energetics to within a few or a few tens of microhartree. This should be compared to about 3–4.5 wall time minutes needed to solve conventional CCSDT equations for the F_2/cc-pVDZ molecule to a microhartree level using codes compatible with our CC(P;Q) implementation (the wall times vary due to varying numbers of CC iterations at different R values). Compared to the purely stochastic calculations, we do not have to stabilize walker/excip populations with energy shifts, since the convergence of CC(P;Q) energies is achieved in the early stages of i-FCIQMC or i-CCMC propagations. This convergence is equally rapid when the cc-pVDZ basis set is replaced by cc-pVTZ and aug-cc-pVTZ (see Fig. 3 and
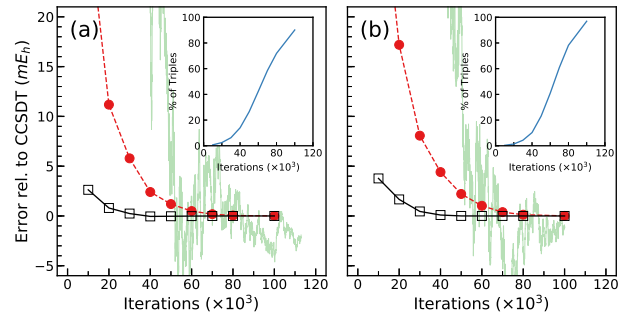

FIG. 3. Same as Fig. 1 for the F_2 molecule with R set at $2R_e$ using the (a) cc-pVTZ and (b) aug-cc-pVTZ basis sets.

the Supplemental Material [31]). For example, when the F_2/aug-cc-pVTZ molecule at $R = 2R_e$ is examined, the differences between the CC(P;Q)$_{\text{EN}}$ and CCSDT energies after 30,000, 40,000, and 50,000 i-FCIQMC iterations, which capture 4, 10, and 23 % of all triples, are 0.454, 0.093, and 0.002 millihartree, respectively. The speedups offered by CC(P;Q) relative to the deterministic CCSDT calculation are about 90, 30, and 10, respectively.

Our final example is the automerization of cyclobutadiene (C_4H_4), examined by CCSDT and other methods in [22]. In this case, T_3 effects, estimated as the difference of the CCSDT and CCSD energies, are not only large, but also difficult to balance. When the cc-pVDZ basis set is employed, they are 26.827 millihartree for the reactant and 47.979 millihartree for the transition state. The CCSDT/cc-pVDZ activation energy is 12.155 millihartree or 7.6 kcal/mol, in good agreement with other reliable estimates [22]. This should be compared to poor values, of about 16–17 kcal/mol, provided by CCSD(T) and other triples corrections to CCSD [22]. The stochastic CC(P;Q) calculations reach a 1 kcal/mol (so-called "chemical") accuracy level, which is largely determined by the results for the challenging multi-reference transition state, after 50,000 $\delta\tau = 0.0001$ a.u. MC steps. We illustrate this by i-FCIQMC-based CC(P;Q)$_{\text{EN}}$ computations. Already after 40,000 i-FCIQMC iterations, which capture 15–22 % of triples, the CC(P;Q)$_{\text{EN}}$ approach recovers the reactant and transition state CCSDT energies and the CCSDT activation energy to within 0.489 and 3.235 millihartree and 1.7 kcal/mol, respectively. The wall times needed to perform such calculations on the aforementioned quad-core workstation are 0.4–0.6 hours in the i-FCIQMC part and 0.6–1.3 hours to complete the CC(P) and $\delta(P;Q)$ calculations, as compared to 19.2–21.9 hours required to obtain the converged CCSDT solutions. After 50,000 i-FCIQMC iterations, which capture 31–41 % of triples, the CC(P;Q)$_{\text{EN}}$ calculations require 3.1–5.9 hours (including MC, CC(P), and $\delta(P;Q)$ steps) to recover the CCSDT reactant and transition state energies and activation energy to within 0.198 and 1.171 millihartree and 0.6 kcal/mol, respectively.

In summary, we showed that by combining the stochastic FCIQMC and CCMC methodologies with the deterministic CC(P;Q) framework one can recover high-level CC energetics based on the information extracted from the early stages of FCIQMC or CCMC propagations, even when electronic quasi-degeneracies become substantial. Although more studies are needed at the various CC and MC theory levels, we believe that the proposed stochastic CC(P;Q) approach opens up new possibilities in the way high-level CC calculations are carried out, being a logical step in exploring FCIQMC and CCMC concepts. Paraphrasing the title of [25], the stochastic CC(P;Q) formalism is a "game of life, death, and annihilation," but based on the results in this letter one may avoid playing much of it and yet know the outcome.

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