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An explicitly correlated approach to basis set incompleteness in full configuration interaction quantum Monte Carlo

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By performing a stochastic dynamic in a space of Slater determinants, the full configuration interaction quantum Monte Carlo (FCIQMC) method has been able to obtain energies which are essentially free from systematic error to the basis set correlation energy, within small and systematically improvable error bars. However, the weakly exponential scaling with basis size makes converging the energy with respect to basis set costly and in larger systems, impossible. To ameliorate these basis set issues, here we use perturbation theory to couple the FCIQMC wavefunction to an explicitly correlated strongly orthogonal basis of geminals, following the $[2]_{R12}$ approach of Valeev *et al.* The required one- and two-particle density matrices are computed on-the-fly during the FCIQMC dynamic, using a sampling procedure which incurs relatively little additional computation expense. The F12 energy corrections are shown to converge rapidly as a function of sampling, both in imaginary time and number of walkers. Our pilot calculations on the binding curve for the carbon dimer, which exhibits strong correlation effects as well as substantial basis set dependence, demonstrate that the accuracy of the FCIQMC-F12 method surpasses that of all previous FCIQMC calculations, and that the F12 correction improves results equivalent to increasing the quality of the one-electron basis by two cardinal numbers. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4762445>]

I. INTRODUCTION

The full configuration interaction quantum Monte Carlo (FCIQMC) method has arisen over the last few years as a way to obtain near exact ground state energies (in the full configuration interaction sense) for Hamiltonians in a given Hilbert space. A range of Hamiltonians have been tackled from molecular^{1–6} to solid-state systems,^{7–10} obtaining accurate correlation energies in Hilbert spaces far beyond the reach of traditional iterative diagonalizers. This is achieved by stochastically sampling the underlying Slater determinant space using a discrete “walker” representation, thereby reducing the computational effort spent on the realisation of the large number of low-weighted amplitudes in the expansion. The price of this stochastic algorithm is the introduction of random errors, which nonetheless can be controlled and reduced as the inverse square-root of the computational effort.

However, it has been known since the early days of electronic structure theory that the necessity for these huge many-body expansions is to a large extent an artifact of the basis functions that are used to represent the wavefunction. The full configuration interaction (FCI) expansion constructs the wavefunction as a linear combination of all possible antisymmetrized spin-orbital products, called Slater determinants.^{11–13} Although the evaluation of matrix elements, and the resulting linear optimisation problem is relatively straightforward and computationally efficient, the size of the determinantal basis scales binomially with the number of spin-orbitals, which is the source of the current restriction on FCI-based methodology. Moreover, since the spin-

orbitals are intrinsically one-electron functions, the Slater determinant basis is ill-suited to some aspects of many-electron correlated motion, specifically those caused by the singular electron-electron interactions at short range. This results in a slow convergence of the electronic energy with the size of the underlying basis, hence exacerbating the binomial bottleneck.

Due to this high scaling with basis size, enlargement of the basis set and subsequent extrapolation is in many cases impossible, particularly for the multi-configurational methods required for strongly correlated systems. As a consequence, for high-level methods, the basis set error is often far larger than the error in the correlation treatment within the basis. Even if convergence with respect to basis size is possible, strong correlation effects are generally considered to be a “small” basis set problem, and thus a similar high-level treatment with increasingly large basis sets is an unnecessary burden. Traditionally, this issue has been dealt with by partitioning the orbital space into a small, active basis in which the wavefunction is constructed from a multiconfigurational FCI-type expansion,^{14–16} before the dynamical, short-ranged correlation is captured via excitations from this wavefunction into a larger, external basis. This is the rationale behind methods such as complete active space second-order perturbation theory (CASPT2),^{17,18} multireference configuration interaction (MRCI),^{19,20} canonical transformation theory,^{21,22} and others.^{23,24} However, these methods can be expensive, and problems can result if the strong correlation is not adequately captured by the active basis.

In this paper, we take a different approach, and attempt to overcome the slow basis set expansion by including geminal functions in the expansion, which perturbatively couple to the FCIQMC wavefunction. Hylleraas’s pioneering work in 1929

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demonstrated that a highly compact form for the short-ranged wavefunction behavior can be found by introducing an explicit dependence on the interelectronic coordinate, r_{12} .^{25–27} This naturally describes the dynamical correlation problem, which covers both the exact form of the “cusp” at $r_{12} = 0$, and the longer ranged Coulomb hole around each electron pair coalescence point. These cusp conditions, derived initially by Kato and co-workers,^{28–30} result from the singularities in the Coulombic electron-repulsion potential, which are balanced by derivative discontinuities in the wavefunction. Neither these cusps, nor the short to medium-range Coulomb holes are well approximated by an expansion of the wavefunction in terms of Slater determinants formed from Gaussian-type orbitals that are centered on the nuclei of the system.

The umbrella of “explicitly correlated” methods covers ways to introduce this explicit dependence on r_{12} into the wavefunction ansatz, including the use of exponentially correlated Gaussians³¹ and the transcorrelated method.^{32,33} These methods have fewer variational parameters to optimize, however, the presence of many-electron (more than two) integrals, and a more complicated optimization problem has restricted these methods to small systems, and their use is not yet routine. An exception to this is the variational Monte Carlo method, where the need for integral evaluation is avoided altogether, by direct stochastic evaluation of the local energy for the optimization of a nonlinear Jastrow form for the wavefunction.³⁴

The R12/F12 methods^{35–37} augment the set of Slater determinants with a small number of determinants that include two-electron geminal functions.^{38–40} The resulting many-electron integrals are avoided, or approximated via resolution of the identity (RI).^{38,39,41–43} The result is a method, which for the same level of theory approaches the basis set limit much more rapidly,⁴⁴ thus greatly reducing the computational effort required for a given target accuracy. This approach has been in active development for many years, and is now at a highly advanced stage for single reference methods, where it is routinely used in a black-box fashion, and present in many quantum chemistry packages. However, apart from some early work,^{45,46} multireference F12 methods have only appeared relatively recently,^{47–55} even though the F12 approach offers great benefits in these cases, where the scaling with respect to basis size is often at its most prohibitive.

In this paper, we extend the stochastic FCIQMC method to include a perturbative coupling from the FCI determinant amplitudes, to a set of Gaussian-type geminal functions which explicitly correlate *all* pairs of orbitals in the FCIQMC orbital basis set (OBS). This is in contrast to single-reference methods, where only the occupied orbitals of the reference determinant are correlated. We follow the *a posteriori* $[2]_{R12}$ approach of Torheyden and Valeev,⁴⁸ where the geminal basis is used to compute a basis set incompleteness correction for the dynamic correlation energy using second-order perturbation theory. The geminal contribution is not optimized, but chosen to satisfy the derivative discontinuity at the electronic cusps, and accurately represent the shape of the Coulomb hole. Furthermore, we neglect the effect of relaxation of the FCIQMC amplitudes and directly use the one- and two-particle reduced density matrices computed from the FCIQMC procedure.

Since the geminals are evaluated at a different level of theory to those FCIQMC amplitudes in the OBS, strict variationality with respect to the FCI complete basis set (CBS) is lost. Nevertheless, we will demonstrate that the perturbative level of theory for geminal amplitudes is sufficiently accurate and that convergence to the FCI-CBS limit is much faster with our hybrid approach, where FCIQMC captures the strong correlation effects from the OBS, while the cheaper, polynomially scaling, but still multireference F12 corrections are used for the remaining dynamic correlation. This “diagonalize-then-perturb” approach offers a balanced description of the electronic correlation, while only requiring the small overhead from accumulating the density matrices on-the-fly.

The geminal basis corrects for the incompleteness in the description of pair correlations, but there remains an incompleteness due to the finite basis for the one-electron description. To remedy this, we modify the $[2]_S$ method of Kong and Valeev⁵⁶ designed to correct for basis set incompleteness in complete active space self-consistent field (CASSCF) wavefunctions to provide a similar multireference *a posteriori* approach to one-particle incompleteness. For single reference methods, it has been demonstrated numerically that the one- and two-particle incompleteness errors are largely decoupled.^{49,57} Therefore, the proposed corrections are independent and can be simply applied additively. When both one- and two-electron corrections have been applied to the FCIQMC energy, we will denote the result FCIQMC-F12.

However, obtaining these corrections is not as straightforward as for many other deterministic methods. The strength of the FCIQMC approach lies in the fact that only a small fraction of the space is occupied at any one iteration, and therefore accurate energies and wavefunctions only emerge after appropriate time-averaging of the walker dynamic. However, explicit averaging of the FCIQMC wavefunction to obtain appropriate density matrices would negate many of the advantages of the method, requiring substantially increased storage and computational costs. Therefore, accumulation of accurate time-averaged one- and two-particle reduced density matrices of the FCIQMC wavefunction required for the corrections must be performed “on-the-fly,” in a manner that neither becomes a substantial computational burden nor reduces the parallelism of the algorithm. In addition, the additional storage requirements of such an algorithm should ideally remain modest, and of course, must not scale with the size of the FCI space.

In this paper, we will demonstrate the potential of the FCIQMC-F12 method by first considering the case of the dissociation of the hydrogen molecule, for which the sampling of the density matrices is trivial. For this simple case we demonstrate some salient features of our approach, and the necessity for multireference F12 corrections in the presence of strong correlation effects. We will then discuss the quality of the on-the-fly stochastically sampled reduced density matrices, and their convergence both with elapsed imaginary time and number of walkers in the space. This issue is important for the application and scope of our approach to larger systems. Finally, a detailed study is performed on the carbon dimer, a strongly correlated molecule, which is chosen since much work with FCIQMC has already been performed for this system

(see Ref. 5). Accurate results for the carbon dimer are presented, and the outlook for the approach considered.

II. METHODOLOGY

A. FCIQMC recap

A brief overview of the FCIQMC method is given here, with more details provided in Refs. 1–8. Assuming a basis of M orthogonal one-particle orbitals $\{p, q, \dots\}$, an explicitly antisymmetric basis of N -electron Slater determinants can be formed, $\{D_i, D_j, \dots\}$, which exactly span the FCI-space. Exact diagonalization of the Hamiltonian in this basis provides the FCI energy (defining the basis-set correlation energy), and wavefunction components on each of the determinantal basis functions $\{C_i, C_j, \dots\}$, though its drawback is that the dimension of this matrix scales factorially with both M and N . In FCIQMC, the description of the determinantal amplitudes is coarse-grained through a discrete “walker” representation of the wavefunction. This allows for a compression of the instantaneous representation of the wavefunction, and corresponding reductions in computational effort and storage. A set of stochastically realised rules are then iteratively applied to each walker, and the energy averaged over these iterations, until the desired convergence is reached.

The master equations governing the stochastic walker dynamic can be derived by starting with the imaginary-time Schrödinger equation,

$$\frac{\partial \Psi}{\partial \tau} = -\hat{H}\Psi. \quad (1)$$

By performing an integration to large imaginary time, τ , the ground-state wavefunction is projected out from the set of all stationary solutions, in keeping with the approach of all projector-based methods. A set of coupled differential equations is found,

$$-\frac{dC_i}{d\tau} = (H_{ii} - E_0 - S)C_i + \sum_{j \neq i} H_{ij}C_j, \quad (2)$$

where C_i are the determinant coefficients, and S is introduced as an energy-offset “shift” parameter, which acts as population control, and provides an estimate of the correlation energy when it is allowed to vary to keep the walker population constant.

The coefficients in Eq. (2) are discretised, and represented as the signed sum of walkers on the determinant. The second term in the equation is simulated each iteration as a stochastically realised spawning criterion between connected determinants, while the first represents a diagonal death step. Annihilation events occur at the end of each iteration between oppositely signed walkers residing on the same determinant. However, brute force application of this procedure will only converge onto the ground state assuming that a system-specific number of walkers is exceeded, since annihilation events need to be numerous enough in order to overcome the “sign problem” present in the sampling of the space. If this is achieved, then at convergence, the signed number of walkers on any determinant will be proportional to their FCI coefficient.

The number of walkers required to achieve convergence to FCI accuracy within small error bars is dramatically accelerated by invoking a systematically improvable approximation, termed initiator or i -FCIQMC, which will be used exclusively in this work. In this, the growth of the occupied determinant space is controlled, such that previously unoccupied determinants can only become occupied if they are spawned onto from a determinant with a population exceeding a preset parameter n_{add} . The rationale behind this is that determinants with weights larger than n_{add} are likely to have their sign established correctly with respect to the rest of the instantaneous wavefunction, and therefore the uncontrolled propagation of noise from competing signed solutions of the problem should be limited. Since the walker population on any determinant is constantly changing, so does the space which can successfully spawn onto the unoccupied determinants, and as such the approximation cannot be written as a simple change to a static Hamiltonian matrix, but rather one which utilises efficient error cancellation within a time-averaged dynamic. The dynamic rigorously converges to the original scheme as the walker number is increased, or n_{add} is reduced, which has been shown in several systems to provide an exponential saving over the original formulation.

The energy can be extracted from the dynamic via a non-variational projection onto a reference wavefunction, D_0 ,

$$E_{\text{proj}} = E_0 + \sum_i \langle D_i | H | D_0 \rangle \frac{\langle C_i \rangle}{\langle C_0 \rangle}, \quad (3)$$

which in this work is chosen to be the instantaneously largest weighted single determinant in the space (which was the Hartree–Fock determinant for geometries close to equilibrium). Alternatively, once the walker population has equilibrated, the value of the shift parameter, S , which renders the propagated FCIQMC wavefunction L^1 norm-conserving, can also be used as an estimate for the correlation energy, which when averaged over imaginary time is denoted E_S . Due to the independence of this estimate from a reference state, it is generally used for the highly multireference stretched geometries in order to obtain smaller error bars.⁶ However, the value of the energy is independent of the specifics of how the energy expectation value is obtained from the dynamic, and within the intrinsic random errors of each estimate, the value of E_S should agree with the projected energy estimate from Eq. (3). As we will see later, it is also possible to calculate another energy estimate from the trace of the reduced Hamiltonian with the sampled two-electron density matrix, but this is not generally the estimate which is used, due to its convergence properties which are discussed later.

B. $[2]_{\text{R12}}$ and $[2]_{\text{S}}$

The $[2]_{\text{R12}}$ and $[2]_{\text{S}}$ methods were developed by Valeev and co-workers as perturbative basis set completeness corrections that can in principle be applied to any electronic state for which the one- and two-particle reduced density matrices are available.^{48,49,56} Here we apply these corrections to the situation where the FCIQMC correlation energy has been determined in a computational basis of spin-orbitals

$\{p, q, r, s\}$. Consider the Mukherjee–Kutzelnigg normal-ordered Hamiltonian

$$\hat{H} = E^0 + \hat{F} + \hat{G}, \quad (4)$$

where $E^0 = \langle 0 | \hat{H} | 0 \rangle$ is the energy of the reference zeroth-order FCIQMC wavefunction $|0\rangle$. The effective Fock operator \hat{F} , in a formally complete one-particle basis denoted by orbital indices $\{\kappa, \lambda\}$, is given by

$$\hat{F} = f_{\kappa}^{\lambda} \tilde{a}_{\lambda}^{\kappa}, \quad (5)$$

$$f_{\kappa}^{\lambda} = h_{\kappa}^{\lambda} + g_{\kappa p}^{\lambda q} \gamma_q^p, \quad (6)$$

where γ_q^p is the one-particle reduced density matrix which spans the one-particle basis of $|0\rangle$, $g_{\kappa p}^{\lambda q} = \langle \kappa p | \lambda q \rangle$ are antisymmetric electron repulsion integrals, $\tilde{a}_{\lambda}^{\kappa}$ are the elementary normal-ordered operators in the Mukherjee–Kutzelnigg sense, and Einstein summation convention is assumed. The zeroth-order Hamiltonian is chosen to be

$$\hat{H}^0 = E^0 + \hat{P} \hat{F} \hat{P} + (1 - \hat{P}) \hat{F} (1 - \hat{P}) + \hat{P} \hat{G} \hat{P}, \quad (7)$$

where \hat{P} projects onto the computational basis $\{p, q\}$, used for the FCIQMC calculation.

The $[2]_s$ energy correction is computed by second-order perturbation theory in a basis of states generated by singly exciting from the reference $|0\rangle$ into complementary auxiliary (CA) orbitals $\{a', b'\}$, orthogonal to the computational basis $\{p, q\}$,

$$|1\rangle = t_{a'}^p \tilde{a}_{p'}^{a'} |0\rangle, \quad (8)$$

$$E_{[2]_s} = f_p^{a'} t_{a'}^q \gamma_q^p, \quad (9)$$

where the amplitudes $t_{a'}^q$ are calculated from the solution of

$$A_{b'q}^{p a'} t_{a'}^q = -\gamma_r^p f_{b'}^r, \quad (10)$$

$$A_{b'q}^{p a'} = \delta_{b'}^{a'} f_r^s (\lambda_{qs}^{pr} - \gamma_s^p \gamma_q^r) + f_{b'}^{a'} \gamma_q^p. \quad (11)$$

$\lambda_{pq}^{rs} = \gamma_{pq}^{rs} - \gamma_p^r \gamma_q^s + \gamma_p^s \gamma_q^r$ is the two-electron cumulant and γ_p^q and γ_{pq}^{rs} are the one- and two-particle density matrices. We also investigated the performance of the zeroth-order Dyall Hamiltonian,⁵⁶ but found that the convergence was less numerically stable.

The $[2]_{R12}$ energy correction is computed by second-order perturbation theory in an internally contracted basis of Gaussian geminal-containing Slater determinants

$$|1\rangle = \frac{1}{4} t_{pq}^{xy} |\tilde{\Gamma}_{pq}^{xy}\rangle, \quad (12)$$

$$|\tilde{\Gamma}_{pq}^{xy}\rangle = \frac{1}{2} \hat{O} R_{\kappa\lambda}^{xy} \tilde{a}_{pq}^{\kappa\lambda} |0\rangle. \quad (13)$$

The operator \hat{O} ensures the strong orthogonality (one-electron orthogonality) condition of the geminal basis to the reference wavefunction, and the matrix elements

$$R_{\kappa\lambda}^{xy} = \hat{S}_{xy} \langle \kappa\lambda | \hat{Q}_{12} f(r_{12}) | xy \rangle \quad (14)$$

are the representation of the projected Gaussian geminals in second quantization. The projector $\hat{Q}_{12} = 1 - P_1 P_2$ is used in order to simplify the working equations, and the rational

generator $\hat{S}_{xy} = (\frac{3}{8} + \frac{1}{8} \hat{p}_{xy})$, where \hat{p}_{xy} interchanges the *spatial* components of the spin-orbitals x and y ,^{58,59} is used to impose the appropriate cusp conditions. The Gaussian geminals $f(r_{12})|xy\rangle$ are defined by the orbital space $\{v, w, x, y\}$, which is chosen to be the full computational basis $\{p, q, r, s\}$ and the correlation factor $f(r_{12})$ is a linear combination of six Gaussians that closely fit an exponential $-\gamma^{-1} \exp(-\gamma r_{12})$,⁶⁰ according to Ref. 61. The $[2]_{R12}$ energy correction is given by the Hylleraas functional

$$E_{[2]_{R12}} = \frac{1}{2} V_{pq}^{xy} t_{xy}^{pq} + \frac{1}{16} t_{rs}^{vw} (B_{vw}^{xy} \gamma_{pq}^{rs} - X_{vw}^{xy} \Phi_{pq}^{rs}) t_{xy}^{pq}, \quad (15)$$

where the many-electron integrals are approximated using standard R12/F12 manipulations and through RI insertions of the basis $\{p', q', r'\}$, defined as the union of the computational basis $\{p, q, r, s\}$ and the CA basis $\{a', b'\}$. This results in the working equations

$$V_{pq}^{xy} = \frac{1}{2} (v_{rs}^{xy} - g_{rs}^{ta'} \gamma_t^u r_{ua'}^{xy} - \frac{1}{2} g_{rs}^{tu} r_{tu}^{xy}) \gamma_{pq}^{rs}, \quad (16)$$

$$\begin{aligned} B_{vw}^{xy} = & -r_{vw}^{rq} f_r^p r_{pq}^{xy} - r_{vw}^{aq} f_a^p r_{pq}^{xy} - r_{vw}^{pq} f_p^{a'} r_{a'q}^{xy} \\ & + r_{vw}^{pa'} \gamma_p^q f_q^r \gamma_r^{sa'} - r_{vw}^{pa'} \gamma_p^q f_a^{b'} r_{qb'}^{xy} \\ & - r_{vw}^{p'a'} f_p^p \gamma_p^q r_{qa'}^{xy} - r_{vw}^{p'a'} \gamma_p^q f_p^{p'} r_{p'a'}^{xy} \\ & + \tau_{vw}^{xy} + \frac{1}{2} x_{vw}^{xy} + \frac{1}{2} x_{vw}^{xy*} + \frac{1}{2} x_{vw}^{xy*} + \frac{1}{2} x_{vw}^{xy*} \\ & - r_{vw}^{p'q'} k_{p'r'}^{r'q'} r_{r'q'}^{xy}, \end{aligned} \quad (17)$$

$$X_{vw}^{xy} = x_{vw}^{xy} - r_{vw}^{ta'} \gamma_t^u r_{ua'}^{xy} - \frac{1}{2} r_{vw}^{tu} r_{tu}^{xy}, \quad (18)$$

$$\begin{aligned} \Phi_{pq}^{rs} = & P(pq)P(rs) (\gamma_p^r \gamma_q^s f_t^u \gamma_u^s + \frac{1}{2} \gamma_t^s f_u^t \gamma_{pq}^{rs} \\ & + \frac{1}{2} \gamma_p^t f_t^u \lambda_{uq}^{rs} - \gamma_p^r f_t^u \lambda_{uq}^{ts}), \end{aligned} \quad (19)$$

where $P(pq)O_{pq} = O_{pq} - O_{qp}$, $|x^*\rangle = (f_p^x + k_p^x)|p'\rangle$, and f and k are the Fock and exchange matrix elements (see Eq. (6)). The geminal integrals are defined through

$$r_{p'q'}^{xy} = \hat{S}_{xy} \langle p'q' | f(r_{12}) | xy \rangle, \quad (20)$$

$$v_{p'q'}^{xy} = \hat{S}_{xy} \langle p'q' | r_{12}^{-1} f(r_{12}) | xy \rangle, \quad (21)$$

$$x_{vw}^{xy} = \hat{S}_{vw} \hat{S}_{xy} \langle vw | f(r_{12})^2 | xy \rangle, \quad (22)$$

$$\tau_{vw}^{xy} = \hat{S}_{vw} \hat{S}_{xy} \langle vw | (\nabla_1 f(r_{12}))^2 | xy \rangle. \quad (23)$$

The geminal amplitudes, t_{xy}^{pq} , are not optimized, but selected to satisfy the coalescence conditions, which due to the presence of the rational generator, reduce to $t_{xy}^{pq} = \delta_{xp} \delta_{yq} - \delta_{xq} \delta_{yp}$. The above equations are essentially those of Kong, Torheyden, and Valeev, adapted for the present purpose. The spin-adapted formalism presented in Ref. 49 recasts the equations in terms of spin-free orbitals, although also introduces

an approximation to remove the appearance of 4-reduced density matrices (RDMs) in the formal theory when calculating the B intermediate. This modification is not expected to change results greatly.⁷¹ Our implementation reduces exactly to the single reference MP2-F12/2C* F12 correction^{62–64} if the diagonal Hartree–Fock density matrices are used. All integrals were computed using the DALTON program⁶⁵ and were combined with stochastically generated one- and two-particle density matrices from FCIQMC in a stand-alone program.

III. DISSOCIATION OF HYDROGEN

In this section, we provide a simple example to illustrate the importance of an F12 correction that takes into account the multireference nature of the underlying wavefunction. The hydrogen molecule provides a simple two-electron system which nonetheless encapsulates many of the problems in *ab initio* quantum chemistry. At equilibrium and compressed bond lengths, dynamic correlation dominates, and both one- and two-electron basis set incompleteness are generally significant. However, as the bond is stretched, the system becomes intrinsically multireference, as unphysical ionic terms in the Hartree–Fock determinant need to be cancelled by a similarly weighted excited determinant. At the dissociation limit, the system reduces to two independent one-electron hydrogen atoms, with no local correlation between the two electrons. By size extensivity, the energy of this system must be exactly $-1 E_h$. However, even if the static correlation is exactly captured, this will still only be achieved in the CBS limit since there remains an incompleteness in the one-electron description, which will simply be twice the error in the Hartree–Fock energy of a hydrogen atom in the same basis. This, therefore, provides a good system to consider both dynamic and static correlation effects, as well as separating the basis set incompleteness in both the one- and two-electron parts of the wavefunction.

In Fig. 1 we contrast the FCIQMC and FCIQMC-F12 binding curves for molecular hydrogen with a range of standard methods, all using the cc-pVDZ basis set. Second-order Møller–Plesset theory (MP2) gives a qualitatively incorrect description for bond lengths greater than $\sim 2.5a_0$ due to the increasingly static correlation effects, whereas the coupled-cluster singles and doubles (CCSD) energies agree exactly with FCIQMC (and FCI) values at all bond lengths, as expected for a two-electron system. However, the CCSD-F12 methods all fail to dissociate H_2 correctly, with errors in the dissociation energy up to $7 mE_h$. The FCIQMC-F12 method achieves the exact dissociation energy to within $\mathcal{O}[\mu E_h]$, which highlights the necessity for an F12 correction that explicitly correlates a multireference wavefunction.

Further insight can be obtained by analysing the individual contributions to the potential energy curves from Fig. 1. In Fig. 2, we plot the $[2]_{R12}$ and $[2]_S$ contributions to the FCIQMC-F12 curve, and contrast them with the equivalent one- and two-body contributions in the MP2-F12, CCSD(F12*), and CCSD-F12b methods. The reason for the failure of the CCSD-F12 methods is that the geminal amplitudes are selected such that they satisfy the coalescence conditions of the first-order wavefunction, that is, they explicitly

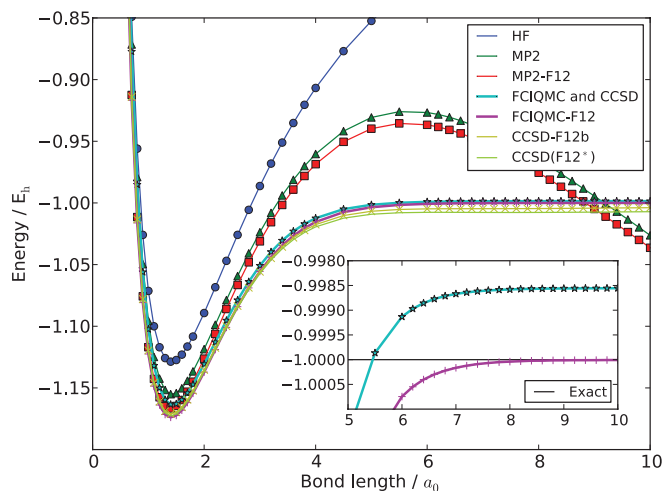


FIG. 1. Binding curves of H_2 in a cc-pVDZ basis. The system takes on a more multireference character as the bond is stretched. Dissociation to two hydrogen atoms should yield an exact energy of $-1 E_h$. However, despite agreement between CCSD and FCIQMC, the single-reference F12 corrections all fail to successfully obtain the correct dissociation limit, with only the fully multireference FCIQMC-F12 energy getting this exactly (error $\mathcal{O}[\mu E_h]$). The individual corrections can be seen in Fig. 2. All calculations used a cc-pV6Z-RI CABS basis, and a γ of $1.0a_0^{-1}$. CCSD calculations were run with MOLPRO.^{67,68}

correlate the Hartree–Fock orbital pairs only. At infinite separation, the hydrogen molecule reverts to a sum of two atomic hydrogen atoms, and since the two electrons are now spatially separated the two-electron F12 contribution should be rigorously zero. This spuriously does not occur for CCSD-F12, because the Hartree–Fock determinant still contains terms with both electrons localized to the same atomic fragment. CCSD-F12 variants where the geminal amplitudes are optimised rather than fixed will dissociate H_2 correctly, since the

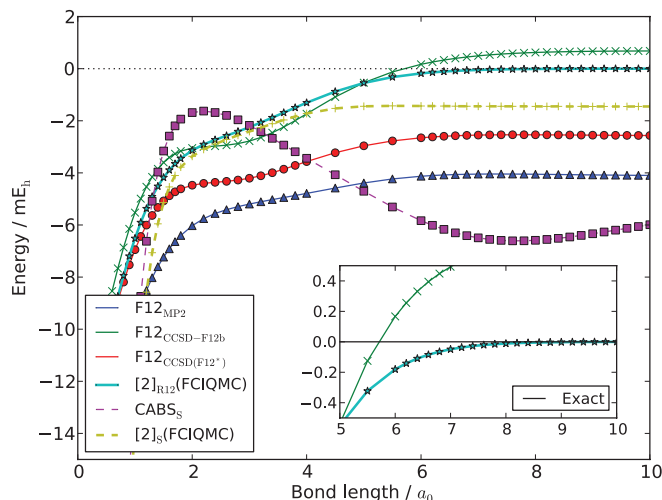


FIG. 2. Individual one- (dashed) and two- (solid) particle corrections to different methods across the dissociation of H_2 , as given in Fig. 1. Although there is no two-particle correlation at dissociation, only the $[2]_{R12}$ F12 correction to the FCIQMC wavefunction correctly goes to zero in this limit. The multireference $[2]_S$ correction for single-particle incompleteness to the FCIQMC wavefunction then provides the remaining energy to give the exact FCIQMC-F12 dissociation limit. The CABS singles approach (CABS_S) overestimates the energy, while the single-reference F12 contributions to the different methods all converge to non-zero contributions.

geminal amplitudes optimise to zero at infinite separation, but these methods suffer from numerical instabilities and geminal basis set superposition errors⁶⁶ and are not recommended. In the FCIQMC-[2]_{R12} approach, all orbital pairs are explicitly correlated and the two-electron correction naturally tends to exactly zero, as required. This example does not intend to highlight a deficiency of CCSD-F12 theory, since for systems of more than two electrons the parent method would also fail for bond-breaking processes, but rather highlight the importance of an explicitly correlated geminal basis composed of more than the occupied Hartree–Fock orbitals in the presence of strong static correlations.

Similar considerations apply to the one-electron basis set incompleteness correction, although this should not now go to zero at the dissociation limit. For increasing bond lengths the FCI basis set incompleteness tends to a sum of the Hartree–Fock basis set errors for the individual hydrogen atoms. Again, the correction for this based on a single Hartree–Fock reference⁶⁸ is shown to be inadequate for long bond lengths where strong correlation effects are large. However, the FCIQMC-[2]_S approach almost exactly corrects for the one-electron error over the whole binding curve, resulting in a total energy at dissociation of $-1 E_h$.

IV. REDUCED DENSITY MATRICES FROM FCIQMC

In order to construct the perturbative coupling to the geminal basis, it is necessary to obtain the one- and two-electron RDM. Much of the benefit of the FCIQMC approach would be lost if the time-averaged wavefunction over the entire FCI space was required in order to construct these, and even an explicit consideration of all occupied determinants connected via the desired RDM each iteration would become impractical when extending the approach to larger systems. Despite this, an accurate extraction of the RDM information from the time-averaged FCIQMC dynamics is essential for this method, while many other important molecular properties, such as nuclear gradients, dipole moments, and polarizabilities can also be obtained from the density matrices via a trace of the observable operator with the appropriate density matrix.

The reduced density matrices over all orbitals in the OBS can be defined in second quantization as

$$\gamma_p^q = \langle \Psi | \hat{a}_p^\dagger \hat{a}_q | \Psi \rangle, \quad (24)$$

$$\gamma_{pq}^{rs} = \langle \Psi | \hat{a}_p^\dagger \hat{a}_q^\dagger \hat{a}_s \hat{a}_r | \Psi \rangle, \quad (25)$$

where the distinction between the one- and two-body matrices is evident from the rank of the tensor. Since the Hamiltonian operator that is sampled during the FCIQMC dynamic contains the same excitation rank as these matrices, it is possible to devise a way to sample the one- and two-body density matrices on-the-fly and stochastically, during the FCIQMC dynamic. The contributions must be appropriately unbiased for the magnitude of the Hamiltonian matrix element between individual connected determinant pairs. The precise manner in which this is done will be described elsewhere. The accumulation of the reduced density matrices begins once the simulation has reached equilibrium and continues for a number of

iterations until sufficient statistical accuracy is obtained, before the matrices are normalized according to their required trace relation. As will be shown, in many cases the density matrices converge rapidly with iterations, resulting in a relatively small computational overhead for their accumulation.

Ignoring potential errors in the description of the wavefunction due to the initiator approximation, two errors can arise due to this on-the-fly sampling of the density matrices. Since they are accumulated via a sampling of the Hamiltonian, it requires that a non-zero Hamiltonian matrix element exists between all pairs of occupied determinants which are connected via one- and two-body excitation operators. If this is not the case, then no walkers can spawn between these determinants, and therefore no contribution can be made to the density matrices from this pair, introducing a bias into the matrices (but not the variational energy from the matrices). Determinants between different symmetry blocks of the Hamiltonian are not connected, however since there will be no weight on determinants outside the currently sampled symmetry block, this does not introduce an error.

The only instance of this criteria being rigorously unfulfilled is in the case of Brillouin's theorem when the one particle basis consists of canonical Hartree–Fock orbitals, and Hamiltonian matrix elements between the Hartree–Fock determinant and all of its single excitations are rigorously zero, despite potentially significant weights on these determinants. To account for this, and improve the description of the RDMs, all connections between the Hartree–Fock determinant and its single and double excitations, are considered explicitly during each iteration. This removes any error due to Brillouin's theorem, and improves the quality of the RDMs with negligible computational overhead. The small possibility that two significantly weighted symmetry-similar determinants are connected via a single or double excitation operator, but with a statistically zero Hamiltonian matrix element between them, remains a potential source of error.

The other possible error from this sampling can arise if instantaneous wavefunction values are used, rather than walker populations averaged in time, i.e., the assumption that $\langle C_i C_j \rangle = \langle C_i \rangle \langle C_j \rangle$, where the averages are over the iterations of the FCIQMC run during accumulation of the density matrices. This assumes no serial correlation between the errors in the determinant populations on D_i and D_j , and therefore enough walkers such that any correlated fluctuations in the amplitudes do not introduce a bias. Since the RDMs are functions of products of these determinant coefficients, this error will not decay to zero simply with increasing sampling time.

However, as opposed to the first error, this bias is systematically improvable, and will rigorously vanish in the limit of a large number of walkers. To ameliorate this error when not at this limit, an averaged walker population over the duration of non-zero occupancy is maintained for each occupied determinant. Since this is only calculated over the instantaneously occupied subspace, it again involves only small additional effort, and weights were not maintained across the whole space. However, an error is still present since this averaged walker population information is lost once a determinant becomes unoccupied. An important question is the rate at which any error decays as the total walker population increases,

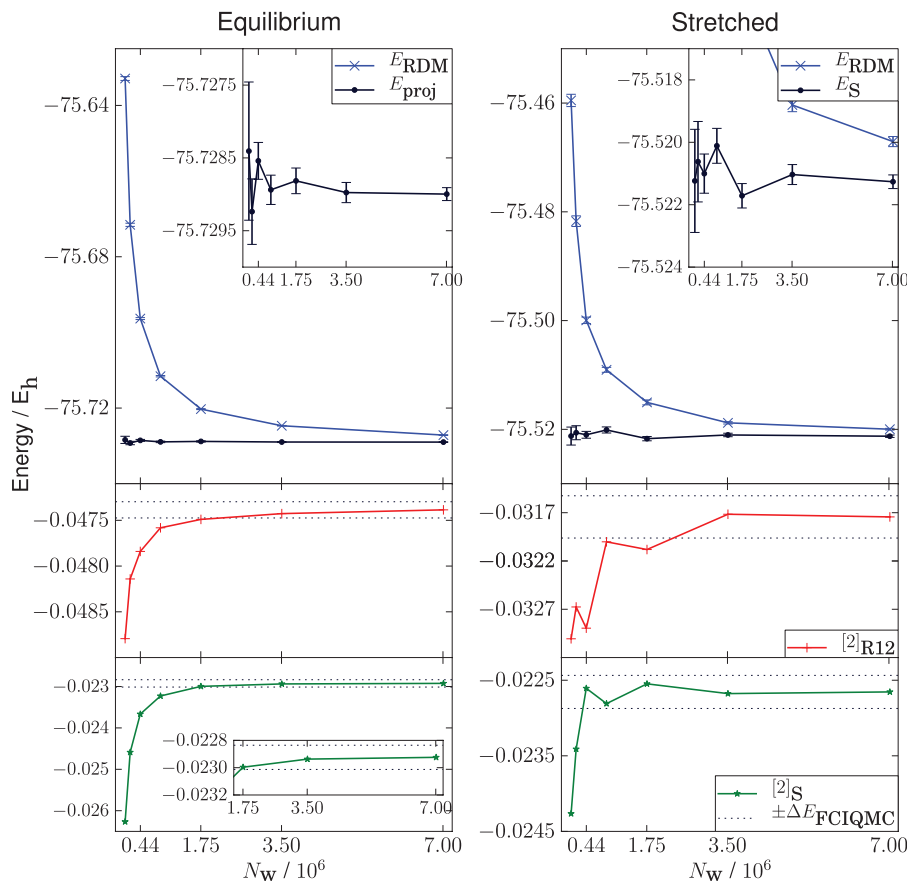


FIG. 3. Convergence of the energy estimates and F12 corrections with increasing walker number, for C_2 in a cc-pVDZ basis set, at equilibrium (1.3 Å) and stretched (7.0 Å) geometries. The dotted lines represent the stochastic errors on the most accurate E_{proj} or E_S values, relative the final $[2]_{\text{R12}}$ and $[2]_{\text{S}}$ results. The density matrices were accumulated over 100 000 iterations.

especially in comparison to the decay of the initiator error and the size of the random errors. This rate of convergence is likely to depend on the specific property that the density matrices are being used to calculate, and in this paper, we will consider the convergence of the error in the calculation of the F12 corrections and energy estimators with increased walker number, as well as the convergence with increased iterations.

A. Convergence of density matrix properties

To investigate the convergence of the density matrices with walker number and imaginary time, we consider both the equilibrium (1.3 Å) and stretched (7.0 Å) geometries of the frozen-core carbon dimer molecule in a restricted Hartree–Fock basis, with a geminal exponent fixed to equal $1.0a_0^{-1}$. These two bond lengths highlight vastly different correlation effects and wavefunctions, to provide contrasting tests for the accuracy of the sampled density matrices. The equilibrium geometry is predominantly single-reference, dominated by the weight at the Hartree–Fock determinant, while the stretched case is highly multiconfigurational, with no single determinant contributing overwhelmingly to the electronic structure. Figure 3 shows the convergence of various estimators used in this work with increasing walkers in a cc-pVDZ basis set, while Fig. 4 extends this to the larger cc-pVTZ basis.

It should be noted that these calculations are independent to the ones calculated in Ref. 5, since angular momentum symmetry was not explicitly included in these calculations. This resulted in a larger space of 2.25×10^{10} symmetry-allowed determinants in the cc-pVTZ basis, although through the use of time-reversal symmetry, the number of distinct N -electron functions is about half this number.

The E_{RDM} energy estimator is calculated from the trace of the two-electron RDM with the reduced two-electron Hamiltonian,

$$E_{\text{RDM}} = \sum_{pqrs} \gamma_{pq}^{rs} k_{pq}^{rs} = \text{Tr}[\gamma k], \quad (26)$$

where

$$k_{pq}^{rs} = \frac{1}{N-1} h_p^r \delta_q^s + g_{pq}^{rs}. \quad (27)$$

This should not be confused with the projected or shift energy estimator from the FCIQMC calculation, which is used to calculate the energy in FCIQMC, and is defined in Eq. (3). Generally, Eq. (26) would define a strictly variational energy for the wavefunction, and be equivalent to the pure estimate $\langle \Psi | H | \Psi \rangle$. However, since the RDM is not explicitly calculated, but rather stochastically sampled, it may not strictly correspond to the FCIQMC wavefunction at all times. This therefore has the potential to break strict N -representability,

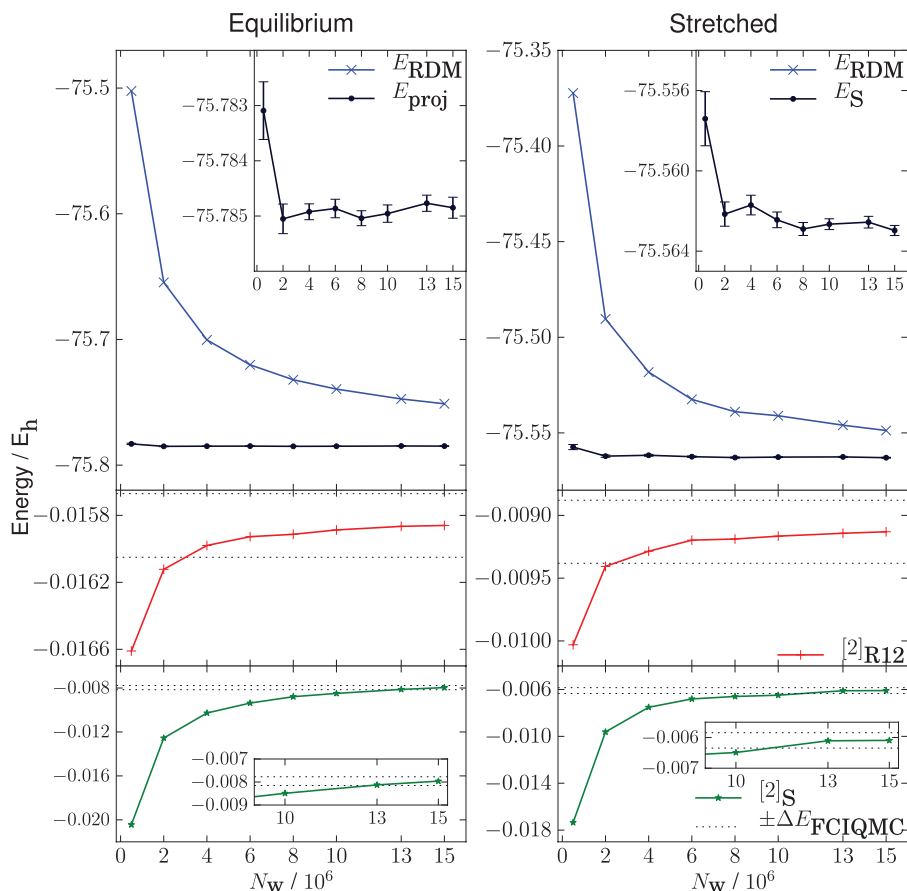


FIG. 4. Convergence of the energy estimates and F12 corrections with increasing walker number, for C_2 in a cc-pVTZ basis, at equilibrium (1.2425 Å) and stretched (7.0 Å) geometries. The dotted lines represent the stochastic errors on the most accurate E_{proj} or E_S values, relative the final $[2]_{\text{R12}}$ and $[2]_S$ results. The density matrices were accumulated over 100 000 iterations.

and thus returns a non-variational energy; however, this is not found in this study and always represents a variational estimate. The effect of the correlated sampling error, compounded by the variational constraint, means that the E_{RDM} energy estimator is found to converge to the FCI energy of the system far slower with respect to walker number compared to the projected or shift energy, as shown in Fig. 3. For this reason, it is not used as an estimate of the FCI basis set energy of the system.

However, this is not found to be the case for the perturbative basis set incompleteness corrections, with $[2]_{\text{R12}}$ and $[2]_S$ based on the sampled density matrices also shown. These indicate convergence to approximately within the stochastic errors of the final FCIQMC energy estimate when the walker number exceeds 3.5×10^6 , for both the equilibrium and stretched geometries. These errors were 0.17 mE_h in the projected energy (E_{proj}) for the equilibrium case and 0.43 mE_h in the shift estimate (E_S) for the stretched case. Intriguingly, the convergence is faster for the multiconfigurational stretched case, although less monotonic. In the stretched case, the two-particle F12 correction is only $\sim 66\%$ of the correction at equilibrium, reflecting the increased separation of the electrons localized to each atom and thus reduced energetic importance of the cusps between them. However, the magnitude of the incompleteness in the one-

electron space is virtually unchanged, and is approximately half the size of the $[2]_{\text{R12}}$ correction.

The convergence in the cc-pVTZ basis (Fig. 4) shows a similar trend, with large errors remaining in the energy from the density matrices (E_{RDM}), while the F12 corrections converge at a much faster rate. Convergence to approximately within the error bars of the FCIQMC energy (0.19 mE_h for the equilibrium case and 0.25 mE_h for stretched) is achieved within a sampling of 15×10^6 walkers. The magnitude of the $[2]_{\text{R12}}$ basis set corrections are only approximately a third of the size in the cc-pVTZ basis compared to the cc-pVDZ basis, while the $[2]_S$ correction is reduced even further to approximately a quarter of its previous size. This reflects the increased correlation captured by FCIQMC in the larger orbital basis, while indicating that this improves the accuracy of the one-body description more than the two-body case.

The observation that the F12 corrections converge much faster than the energy estimate from the density matrices can be rationalized by considering the limiting case of a diagonal Hartree–Fock density matrix. This would recover the single-reference F12 and CABS singles corrections of MP2, which are already quite accurate at equilibrium, whereas the correlation energy computed using E_{RDM} is by definition zero. It is key to note that in both cases, the convergence of the F12 corrections with walker number to within the stochastic

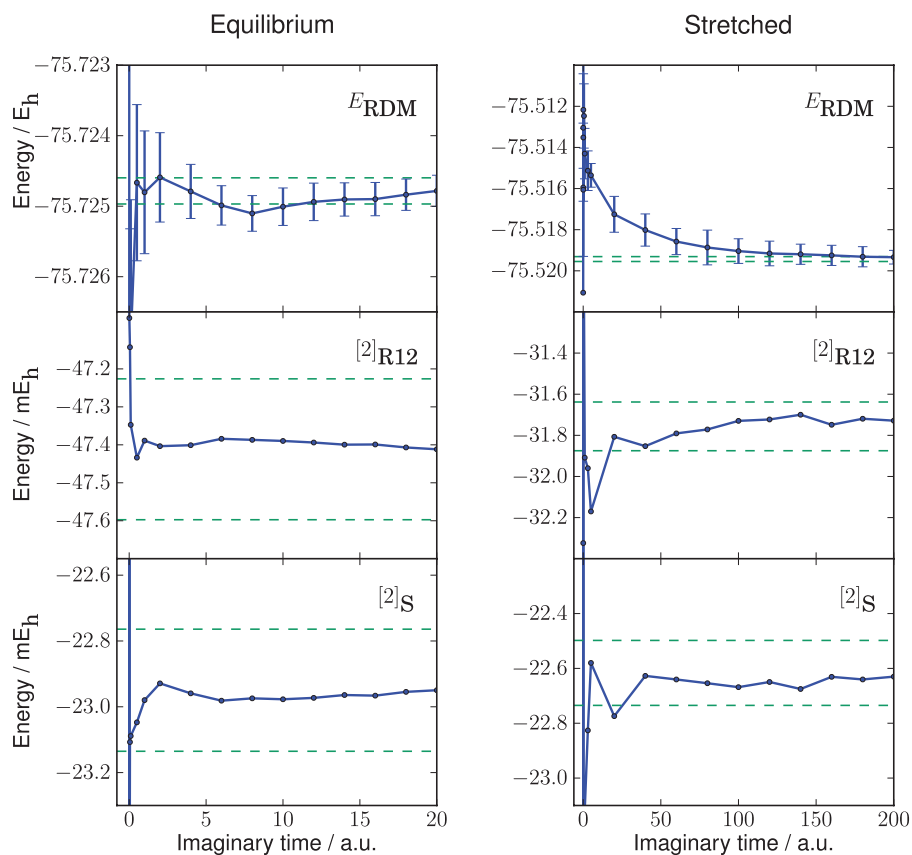


FIG. 5. Convergence of the energy estimates with imaginary time spent sampling the density matrices for C_2 in a cc-pVDZ basis for both equilibrium (1.3 Å) and stretched (7.0 Å) geometries. About 3.5×10^6 walkers sampled the space. Dotted lines show typical error bars in FCIQMC projected energy and shift, taken to be the same as in Fig. 3.

errors of the *i*-FCIQMC energy is not significantly slower than the number of walkers required to acceptably remove the effects of the initiator approximation in the FCIQMC energy estimate, and therefore the additional expense of calculating the F12 corrections is not a large fraction of the overall computational cost.

Another key consideration is the convergence of the F12 corrections with respect to sampled imaginary time. Figure 5 shows this for the cc-pVDZ basis, again at both equilibrium and stretched geometries. In contrast to the convergence with walker number, significant differences exist between the two geometries, with the more multiconfigurational wavefunction at stretched geometry requiring many more iterations to reach energy convergence to within typical stochastic error bars of the *i*-FCIQMC energy estimator. Despite this, the number of iterations required to sample the density matrices to obtain this accuracy in the F12 estimates is again not generally more than required to obtain typical error bars in the calculation of the FCIQMC energy estimate ($\mathcal{O}[10^{-4}]E_h$). Although not shown, the cc-pVTZ basis exhibits a similar convergence.

V. THE CARBON DIMER

The carbon dimer has been the focus of a recent FCIQMC investigation, where its strong correlation effects, state crossings of the same Abelian symmetry group, avoided crossings and large basis set incompleteness provided a stringent test of

any method.⁵ Despite enlargement of the basis to quadruple-zeta quality, it was evident that large basis set errors remained. This is now tackled within the framework of the explicitly correlated approach in order to improve upon these results. Following the convergence investigations shown in Figs. 3 and 4, the cc-pVDZ and cc-pVTZ C_2 binding curves were calculated with FCIQMC-F12 using 3.5×10^6 and 13×10^6 walkers, respectively, for each geometry. The 2-RDM was stochastically constructed once each simulation reached constant walker mode. Angular momentum symmetry is not explicitly imposed in our calculations. Therefore, to avoid complications arising from state crossings and metastable convergence to excited states,⁵ we considered bond lengths less than 1.6 Å where the ground $X^1\Sigma_g^+$ state is dominant, as well as geometries near dissociation with bond lengths more than five times the equilibrium.

In Fig. 6 we plot the deviation between FCIQMC and FCIQMC-F12 energies with various basis sets and our reference FCIQMC-F12/cc-pVTZ values, as a function of bond length. In Table I we present non-parallelity errors (NPE), defined as the maximum absolute deviations over the range of geometries considered. The F12 corrections reduce the NPE of the FCIQMC/cc-pVDZ method by more than a factor of seven, which is comparable with the NPE of the FCIQMC/cc-pVQZ energies. However, the cc-pVQZ basis requires over 30×10^6 walkers to converge the FCIQMC energy,⁵ even when angular momentum symmetry is utilised. In contrast,

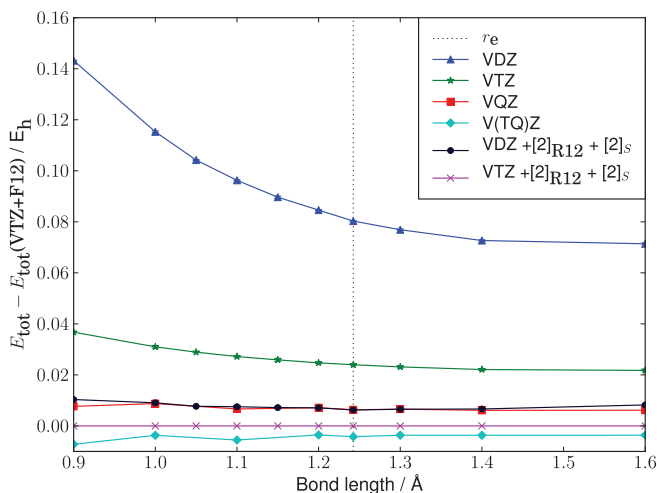


FIG. 6. The errors relative to the FCIQMC-F12 results in the cc-pVTZ basis, for the C_2 binding curves calculated using the cc-pVDZ, cc-pVTZ, and cc-pVQZ basis sets, as well as the cc-pVDZ energies with F12 corrections and extrapolated cc-pV(TQ)Z energies.⁶⁹ Only the 0.9–1.6 Å region is shown, as all these calculations converge onto the $X^1\Sigma_g^+$ state. With F12 corrections, the NPE across the entire cc-pVDZ binding curve is reduced from 86.8(4) to 12.3 mE_h. The NPEs are compared in Table I. The vertical line denotes the equilibrium geometry.

the cc-pVDZ basis only requires a tenth of this number, even without the additional symmetries, highlighting the saving achieved with the hybrid F12 approach within FCIQMC. The effect of including the whole range of bond lengths is unlikely to affect the NPEs, since the dominant basis set incompleteness error is found at equilibrium and compressed geometries, where the electrons are in close proximity, and dynamical correlation is at its largest.

It is this fact which makes the calculation of the dissociation energy so sensitive to basis set incompleteness. To compute this quantity, we performed a calculation of the system at a dissociated geometry of 6.21265 Å. This bond length represents a stretching to five times the experimental equilibrium geometry, which has been shown to provide an energetic dissociation limit within the given random error bars, as well as being consistent with previous studies.⁵ This was chosen rather than twice the atomic system, since it provides a highly

TABLE I. The non-parallelity error and dissociation energies obtained from each of the C_2 binding curves. The uncorrected cc-pVQZ results were taken from Ref. 5. The NPE refers to the non-parallelity error across the $X^1\Sigma_g^+$ state up to geometries of 1.6 Å. The experimental dissociation energy was taken from Ref. 70, and includes a correction to account for core-valence correlation. A standard deviation random error in the final digit is indicated by the number in parentheses. These are not included in the F12 corrected values, but can be expected to have random errors of at least the same magnitude of those in the uncorrected energies.

Basis	NPE (mE _h)	D_e (kcal mol ⁻¹)
cc-pVDZ	86.8(4)	130.0(1)
cc-pVTZ	21.0(6)	139.9(3)
cc-pVQZ	4.9(6)	143.3(2)
cc-pVDZ+F12	12.3	142.3
cc-pVTZ+F12		145.3
Experimental		146.9(5)

multiconfigurational state with which to test the application of the corrections, and allows for a test in the uncorrected FCIQMC values for any size-consistency error relative to the atomic reference systems. The results can be seen in Table I, compared to the experimental dissociation value which is approximately corrected for zero-point energy and core-valence correlation effects. A similar trend to the NPEs is observed, with the F12 corrected FCIQMC value in a cc-pVDZ basis achieving accuracy just shy of the uncorrected cc-pVQZ result.

Despite the large improvement of the cc-pVTZ basis FCIQMC-F12 result, the dissociation energy is still not within chemical accuracy of the experimental value. When taking into account random errors of the FCIQMC method, as well as uncertainty in experimental results, these values differ by 1.6(6) kcal mol⁻¹. From a calculation of the all-electron cc-pVTZ FCIQMC-F12 energy at the experimental equilibrium and fully dissociated geometries, the error is reduced to 0.92(53) kcal mol⁻¹, with the approximate core-valence correction neglected. Although this improves the final dissociation energy to within “chemical accuracy,” it is yet to be seen whether remaining basis set error (such as a need for additional diffuse functions within the F12 framework), other neglected effects, or experimental ambiguity can account for the remaining discrepancy between the two values. However, it is clear from this, and other studies,⁷⁰ that achieving chemical accuracy for this system is exceedingly difficult, where strong correlation, as well as significant basis set incompleteness can cause severe errors.

VI. SUMMARY AND CONCLUSIONS

In this paper we use *a posteriori* $[2]_{R12}$ and $[2]_S$ approach^{48,49,56} in order to account for basis set incompleteness within FCIQMC. This allows for perturbative excitations from the sampled FCIQMC wavefunction into a space of strongly orthogonal geminal functions, via the two-body reduced density matrix which is accumulated on-the-fly. The basis set error in the one-particle space is accounted for via an adaptation of the $[2]_S$ method designed for incompleteness in CASSCF. It is shown that the need for an F12 correction which can correlate a multireference zeroth order wavefunction, is crucial in strongly interacting systems. The convergence of the F12 properties with respect to both increasing walker number and sampling time of the density matrix is investigated, and found to converge at a similar rate to that of the projected energy estimate used in *i*-FCIQMC. This was the case for both the primarily dynamically correlated carbon dimer at equilibrium geometry as well as the highly multiconfigurational stretched geometry. A relatively modest increase in computational effort was required to calculate these F12 corrections, and therefore a large saving was achieved by using the corrections to reduce the basis set error with FCIQMC in converged calculations.

This machinery was then used to treat the carbon dimer at a variety of bond lengths and basis sets, in order to quantify the benefit of the F12 corrections. This system was the subject of a previous investigation, where remaining basis set error, even in quadruple zeta basis sets, prevented convergence

to within chemical accuracy. In keeping with other studies, the F12 corrections were found to provide a gain of close to two cardinal numbers in the basis set when considering non-parallelity errors and dissociation energies, and provided a balanced description of both dynamic and strong correlation effects at equilibrium and stretched geometries. This enabled the calculation of the dissociation energy to within chemical accuracy once core electron correlation was explicitly taken into account. In the future, we hope this approach will allow us to tackle a range of strongly correlated systems, without requiring large computational basis sets for the FCIQMC calculation. This approach, however, does not allow for a relaxation of the FCIQMC wavefunction due to the presence of the geminal functions. A future aim will be to compare this approach with an alternative *a priori* transcorrelation of the Hamiltonian,^{32,55} as well as more traditional CASPT2 and MRCI techniques.

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