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ABSTRACT

Developing global, high-dimensional potential energy surfaces (PESs) is a formidable task. Beside the challenges of PES fitting and fitting set generation, one also has to choose an electronic structure method capable of delivering accurate potential energy values for all geometries in the fitting set, even in regions far from equilibrium. Such regions are often plagued by Hartree–Fock (HF) convergence issues, and even if convergence is achieved, self-consistent field (SCF) procedures that are used to obtain HF solutions offer no guarantee that the solution found is the lowest-energy solution. We present a study of the reactant regions of $\text{CH}_3\text{OH} + \text{OH}^\cdot$, $\text{C}_2\text{H}_6 + \text{F}^\cdot$, and $\text{CH}_3\text{NH}_2 + \text{Cl}^\cdot$, where the SCF procedure often converges to a higher-energy state or fails to converge, resulting in erratic post-HF energies and regions where no energy is obtained, both of which are major obstacles for PES development. We introduce a pragmatic method for automatically finding better HF solutions (dubbed ManyHF) and present evidence that it may extend the applicability of single-reference methods to some systems previously thought to require multireference methods.

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One has to overcome three major challenges in order to develop useful reactive global potential energy surfaces (PESs): accurately fitting a potential energy function to a set of molecular geometries and their energies, choosing a suitable set of molecular geometries,¹ and calculating sufficiently accurate potential energy values at the chosen geometries. While all three are active areas of research, the first two are typically adequately addressed by permutationally invariant polynomials^{2–5} (or neural networks^{6–9} and their combinations^{10–12}) and automated PES development tools,^{13–20} respectively.

This leaves the issue of calculating sufficiently accurate potential energies as the main obstacle to the rapid automated development of PESs. In almost all instances, the source of potential energies is a quantum chemical calculation, typically with a single-reference (SR) correlated *ab initio* method. Indeed, in many cases, the combination of an explicitly correlated coupled cluster calculation with single, double, and perturbative triple excitations [CCSD(T)-F12]^{21,22} and at most a triple-zeta basis set is

both computationally affordable and sufficiently accurate for PES development.^{23–26} Corrections for basis set incompleteness, inner-shell correlation, and relativistic effects can be added in a straightforward manner, if needed, to yield efficient composite schemes.^{24,26,27} In some cases, even deficiencies in CCSD(T) can be efficiently addressed via composite schemes that include Brueckner coupled-cluster calculations.²⁸

Yet there is a single point of failure for all such schemes: they all use a single Hartree–Fock (HF) wavefunction as their reference. Should the HF reference be a poor approximation of the exact ground state wavefunction at a particular geometry, the accuracy of SR methods can be severely degraded. Furthermore, if the self-consistent field (SCF) iterations fail to converge to a HF solution, all further calculations become impossible. These issues are of particular concern for developing global PESs, where it is necessary to include a substantial number of geometries far from equilibrium in the fitting set, to properly sample bond-breaking regions.

Conventional wisdom suggests that one should switch to multireference (MR) methods if the HF reference is poor or difficult to obtain. While it is certainly possible and sometimes necessary to develop a PES using MR methods,²⁹ they come with a number of drawbacks that become ever more prominent as we aspire to develop PESs for larger systems and more complicated reactions that have multiple competing mechanisms leading to different sets of products.

Perhaps the two most severe downsides of MR methods are the difficulty of choosing an active space suitable for all of the 10^4 – 10^5 geometrically diverse points required for fitting a global reactive PES, and the lack of a practical method for accurately incorporating dynamic correlation, especially triple excitations. As a consequence, PESs developed using MR methods often struggle to match the accuracy of reaction energies seen for CCSD(T)-based PESs.²⁹

Clearly, a method that extends the applicability of SR methods would be desirable. So far, such endeavors have mostly approached the breakdown of SR correlated methods from the direction of the correlated method, and a vast array of schemes have been proposed to improve the performance of traditional SR methods at geometries with multireference character.^{30–38} At the same time, the possibility of improving the HF reference itself has seen little attention, especially in the context of PES development, where we could only find a single example.³⁹

While manually ensuring that all fitting points have converged to the desired electronic state is obviously unfeasible, and the worst case computational complexity of the HF problem (NP-complete⁴⁰) makes a hypothetical HF solver that has guaranteed convergence to the global minimum impractical, it may still be possible to improve results for chemically relevant systems at an affordable computational cost. This is clearly demonstrated in Ref. 39, where Liu *et al.* reported the successful development of a single-reference reactive PES, for the triplet state of the OH· + HOO· system, by always picking the lowest HF solution from three HF calculations initialized with cationic, neutral, and anionic guesses.

Here, we present three doublet systems where standard SCF methods struggle to find the lowest-energy restricted open-shell HF (ROHF) solution, and as a result, the corresponding MP2 and CCSD(T)-F12b energies are unreliable. We propose that this issue can be greatly alleviated by starting the desired HF calculation from multiple different sets of initial orbitals, generated via multiple approaches, as described below. We present results from one-dimensional (1D) scans and randomized samplings of the reactant regions, and the communication ends with a summary and conclusions.

All quantum chemical computations have been performed with the Molpro 2015.1.44^{41–46} package, and the ManyHF method has been implemented as a specially crafted Molpro input file, which is available with a detailed explanation in the [supplementary material](#). Here, we refrain from discussing most of the program-specific implementation details, and focus on the principles of the ManyHF method, which should be portable to any other quantum chemical program system with some development effort.

The essence of a ManyHF-enhanced correlated calculation is that the HF reference demanded by the correlated method is obtained by choosing the lowest-energy HF solution out of multiple instances of the desired HF calculation, each started from a different set of initial (“guess”) orbitals. This is essentially an application of the

well-known “multistart” global nonlinear optimization strategy of repeating a local optimization from different initial conditions, and somewhat similar in spirit to the randomized orbital perturbation method of Vaucher and Reiher,⁴⁷ and can be seen as an extension of the method used by Liu *et al.*³⁹

In addition to trying different sets of initial orbitals, we also attempt to find lower HF solutions by changing the algorithm used to solve the HF problem. In this work, we use the multiconfigurational-SCF (MCSCF) module^{48,49} of Molpro to perform single-configurational HF calculations with a markedly different convergence acceleration algorithm, potentially converging to better HF solutions. In other quantum chemistry packages, activating second-order SCF (SOSCF) or other alternative algorithms may have a similar effect.

In this work, we choose the final ROHF solution out of 14 candidates, derived from seven different sets of guess orbitals. The selection of the seven methods used to generate guesses was largely an empirical process. We experimented with various combinations of the common *ad hoc* tricks (such as those found in the Molpro manual) employed by quantum chemists when faced with obstinate SCF calculations, until we arrived at a minimal subset of methods that always finds the lowest known ROHF solution for the tested geometries of the three systems discussed in this work.

As a concrete example, Fig. 1 presents a simplified overview of a ManyHF-enhanced RCCSD(T)-F12b/aug-cc-pVDZ calculation.

First, five Kohn–Sham density functional theory (DFT) calculations are performed. The initial (“guess”) orbitals for these Kohn–Sham (KS) calculations are generated by the atomic density guess method⁵⁰ of Molpro:

1. Restricted open-shell Kohn–Sham (ROKS) with the Perdew–Burke–Ernzerhof (PBE) functional⁵¹ and the MINAO⁵² basis set [denoted as ROKS(PBE)/MINAO].
2. ROKS with the PBE0 functional⁵³ and the MINAO basis set [denoted as ROKS(PBE0)/MINAO].

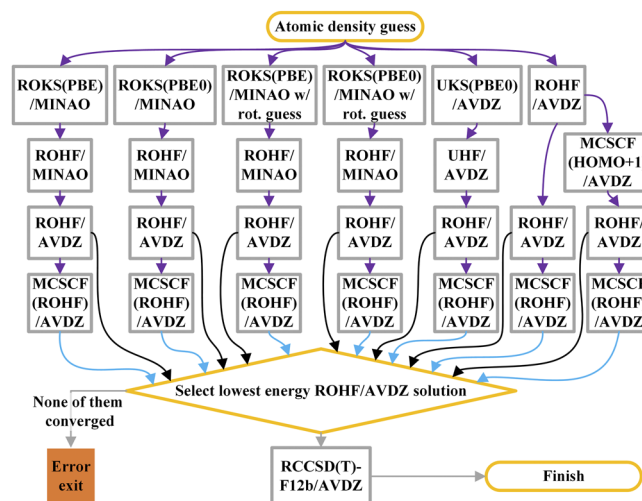


FIG. 1. Simplified flowchart of an RCCSD(T)-F12b/AVDZ calculation that utilizes the ManyHF method to obtain its ROHF reference. The purple arrows indicate the passing of intermediate orbital sets, black arrows indicate the primary candidates, and light blue arrows indicate the secondary candidates.

3. A second ROKS(PBE)/MINAO calculation, with the highest two occupied orbitals (HOMO and HOMO-1) of the guess swapped before the SCF iterations.
4. A second ROKS(PBE0)/MINAO calculation, with the HOMO/HOMO-1 swap.
5. Unrestricted KS (UKS) with the PBE0 functional and the aug-cc-pVDZ basis set^{54,55} [denoted as UKS(PBE0)/AVDZ].

The final orbitals from these calculations (even if they fail to converge) are then used as the initial orbitals for subsequent HF calculations, leading to the first five ROHF/AVDZ candidates.

The sixth candidate is an ordinary ROHF/AVDZ calculation started from the atomic density guess (which is the default), while the seventh is an MCSCF calculation where the active space is set to include all non-core electrons and all non-core occupied orbitals, plus the LUMO. The latter MCSCF calculation is started from the final orbitals of the ordinary ROHF/AVDZ, and is followed by a ROHF/AVDZ calculation which starts from the MCSCF natural orbitals, as shown in Fig. 1.

All seven ROHF/AVDZ results are considered as candidates for the best HF solution, both as is (primary candidates), and after passing them through the MCSCF module in ROHF mode (secondary candidates), and the lowest energy solution is then used as the reference wavefunction for the desired correlated method.

We note that ManyHF, as described in this work, can be interpreted as a particularly complicated but very robust SCF initial guess algorithm, which explores SCF solution space and improves upon the standard atomic density guess. While it remains to be seen how ManyHF compares to more recent SCF guess methods (such as the superposition of atomic potentials (SAP) and superposition of atomic densities natural orbitals (SADNO) methods of Lehtola⁵⁰), we are not convinced that any single initial guess method would match the robustness of a ManyHF-like approach that tries multiple guesses.

Nevertheless, one can imagine a less complicated ManyHF-like method that simply tries all standard SCF initial guess methods and

selects the best solution. We have not pursued this direction due to a paucity of guess methods implemented in Molpro.

In this work, we demonstrate the necessity and utility of the ManyHF method by examining the energy differences between naïve and ManyHF-enhanced single-reference correlated calculations at geometries sampled from the reactant regions of three doublet systems: $\text{CH}_3\text{OH} + \text{OH}^-$, $\text{C}_2\text{H}_6 + \text{F}^-$, and $\text{CH}_3\text{NH}_2 + \text{Cl}^-$. For each reaction, in addition to 1D scans, we used a combination of random displacements and rotations,⁵⁶ followed by the removal of excessively similar geometries to sample the reactant regions. Details about the generation of these geometry sets are available in the [supplementary material](#).

The final number of geometries generated by the random sampling was 4067, 4647, and 5107, respectively, for the three systems. The potential energy values at these geometries were calculated at the RMP2/AVDZ level using both a naïve ROHF reference (resulting from the default guess method and convergence thresholds of Molpro) and the best ROHF reference ManyHF could find.

The potential energies of the 1D scans were obtained similarly at the RCCSD(T)-F12b/AVDZ level. It should be noted that all geometries were processed as completely independent single-point calculations; thus, every point of the scan has to find the correct HF solution without reusing the orbitals of a neighboring point. While this is contrary to common practice when it comes to computing 1D scans, it is more representative of what happens during the development of a PES.

Figure 2 shows the potential energy curves (PECs) as the OH⁻ approaches the methyl and hydroxyl hydrogens of MeOH with its oxygen facing said H-atom, calculated with naïve- and ManyHF-ROHF referenced RCCSD(T)-F12b/AVDZ.

At large separations, PECs agree with negligible difference, then suddenly separate as naïve calculations start converging to higher ROHF solutions, resulting in errors in RCCSD(T)-F12b energies in excess of 100 kcal/mol in both examples, clearly an unacceptable result. Furthermore, a segment of the PEC for the approach of the hydroxyl hydrogen [Fig. 2(b)] is lost to HF or CC non-convergence.

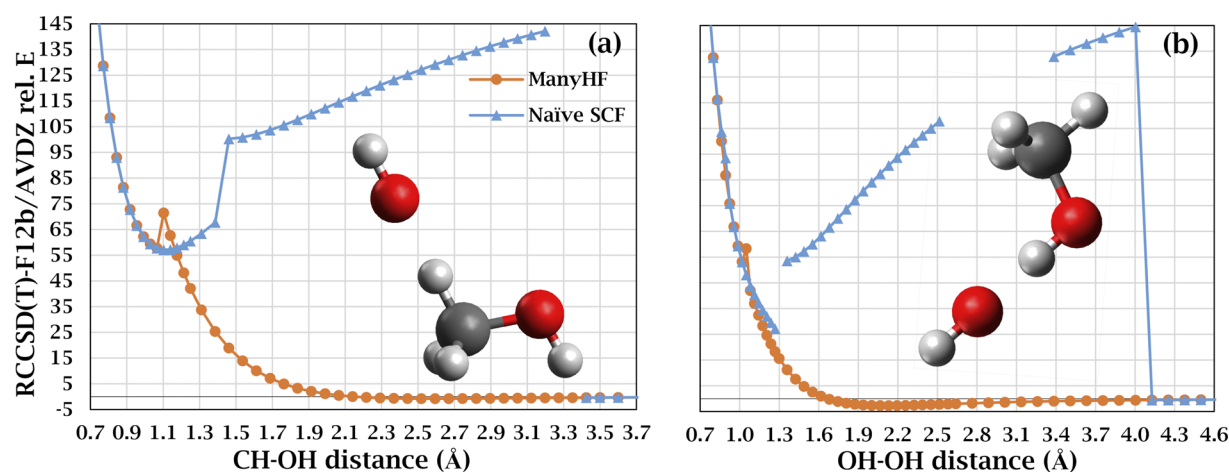


FIG. 2. RCCSD(T)-F12b/AVDZ potential energies relative to free $\text{CH}_3\text{OH} + \text{OH}^-$, calculated using ROHF references from the default SCF procedure and ManyHF, as a function of OH⁻ distance from a methyl hydrogen [panel (a)] and hydroxyl hydrogen [panel (b)]. The energies are in kcal/mol, and the panels have the same vertical scale.

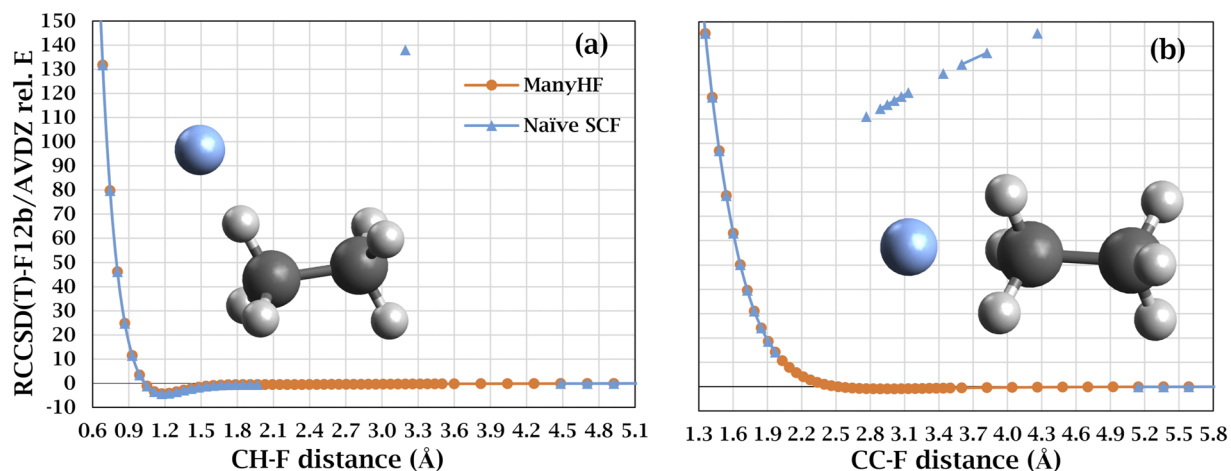


FIG. 3. RCCSD(T)-F12b/AVDZ potential energies relative to free $C_2H_6 + F\cdot$, calculated using the ROHF references from the default SCF procedure and ManyHF, as a function of F- distance from a hydrogen [panel (a)], and a carbon atom [panel (b)]. The energies are in kcal/mol, and the panels have the same vertical scale.

While Fig. 2(a) shows a discontinuity even in the ManyHF-enhanced energies at around 65 kcal/mol in the repulsive region where two HF solutions cross, its impact on PES development is expected to be small. The jump in energy is attributable to the nonvariational nature of RCCSD(T).

The PECs corresponding to F- approaching the hydrogens of C_2H_6 , both along a C-H axis [Fig. 3(a)] and along the C-C axis [Fig. 3(b)], tell the same story. While the ManyHF-enhanced PECs are continuous and appear to be reasonable, the naïve calculations yield unacceptable PECs, with numerous convergence failures and spurious energies.

Looking at the geometries sampled from the reactant regions, out of the 4067, 4647, and 5107 geometries generated for the three systems, we were able to obtain an RMP2 energy for all, except four geometries of $MeNH_2 + Cl\cdot$. Geometries where the RMP2/AVDZ energy derived from the best ROHF solution was greater than 400 kcal/mol (relative to free reactants) will be excluded from further discussion, leaving us with 3012, 4173, and 4122 geometries.

For the $MeOH + OH\cdot$ system, 444 points (14.7%) required the use of ManyHF to achieve SCF convergence, this figure is 1118(26.8%) and 449(10.9%) for the $EtH + F\cdot$ and $MeNH_2 + Cl\cdot$, respectively, clearly indicating that one cannot rely on the default

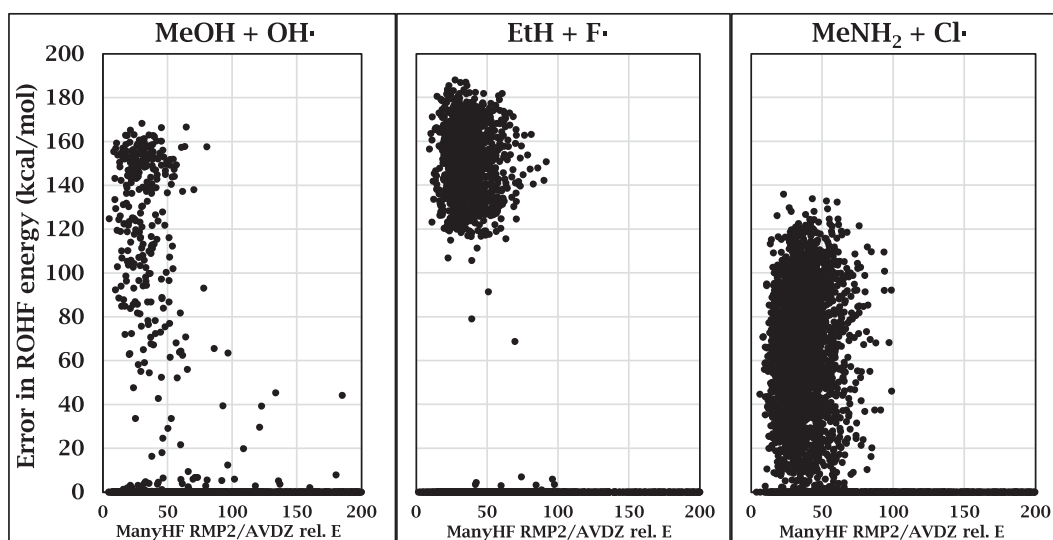


FIG. 4. Errors in the naïve ROHF/AVDZ energies as a function of the ManyHF-enhanced RMP2/AVDZ energies relative to free reactants, at geometries sampled from the reactant regions. All energies are in kcal/mol, and the panels have the same vertical scale.

settings of standard SCF solvers and ordinary initial guess methods to robustly achieve SCF convergence for these challenging open-shell systems.

Looking beyond non-convergence, convergence to a higher energy solution is similarly common. Figure 4 shows results from the random sampling of the entrance channels of the three systems, demonstrating that SCF misconvergence causes pervasive errors in HF energies even in the <50 kcal/mol energy ranges. Such errors are generally not correctable with single-reference correlated methods and are a major obstacle for PES development.

The ManyHF method for finding better, lower energy HF solutions by performing an empirically determined set of preliminary SCF calculations to generate multiple initial guesses was described and its utility demonstrated on three doublet systems: CH₃OH + OH·, C₂H₆ + F· and CH₃NH₂ + Cl·. ManyHF appears to be able to find better ROHF solutions without specialized or exotic SCF solvers, such as SCF-metadynamics⁵⁷ or semidefinite programming.^{58,59}

Evaluating the potential energies at geometries sampled from the reactant regions via 1D scans and filtered random rotation-displacement combinations revealed major deviations in ROHF and RCCSD(T)-F12b energies computed naïvely with a typical SCF program that starts from an atomic density guess, resulting in errors in excess of 100 kcal/mol in chemically important regions of the configuration space. Rectifying such spurious energies stemming from SCF misconvergence is expected to be essential for the successful development of single-reference potential energy surfaces for the three systems discussed, and ManyHF seems to be a pragmatic method of achieving that.

Efforts to develop a global PES for the MeOH + OH· system using ManyHF are currently underway, and we expect that ManyHF-like methods may enable the development of PESs for a wide range of systems with challenging electronic structures, leading to advances in the understanding of the dynamics of radical reactions.

See the [supplementary material](#) for an annotated example ManyHF Molpro input file, a detailed description of this input file with additional figures, details about the generation of the 1D scans and the sampling of the reactant regions, energy distribution histograms for the reactant region geometries, practical notes regarding running ManyHF input files and hyperlinks to Zenodo datasets containing source code, and the geometries of the 1D scans and reactant region samples in XYZ format.

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AUTHOR DECLARATIONS

Conflict of Interest

The authors have no conflicts to disclose.

DATA AVAILABILITY

The data that support the findings of this study are openly available in Zenodo at <http://doi.org/10.5281/ZENODO.5575910>; <http://doi.org/10.5281/ZENODO.5576085>; and <http://doi.org/10.5281/ZENODO.5576827>, Refs. 5, 6, and 8 found in the [supplementary material](#) and from the corresponding authors upon reasonable request.

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