

Steering Orbital Optimization out of Local Minima and Saddle Points
Toward Lower Energy

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(Dated: 3 January 2017)

The general procedure underlying Hartree–Fock and Kohn–Sham density functional theory calculations consists in optimizing orbitals for a self-consistent solution of the Roothaan–Hall equations in an iterative process. It is often ignored that multiple self-consistent solutions can exist, several of which may correspond to minima of the energy functional. In addition to the difficulty sometimes encountered to converge the calculation to a self-consistent solution, one must ensure that the correct self-consistent solution was found, typically the one with the lowest electronic energy. Convergence to an unwanted solution is in general not trivial to detect and will deliver incorrect energy and molecular properties, and accordingly a misleading description of chemical reactivity. Wrong conclusions based on incorrect self-consistent field convergence are particularly cumbersome in automated calculations met in high-throughput virtual screening, structure optimizations, \textit{ab initio} molecular dynamics, and in real-time explorations of chemical reactivity, where the vast amount of data can hardly be manually inspected. Here, we introduce a fast and automated approach to detect and cure incorrect orbital convergence, which is especially suited for electronic structure calculations on sequences of molecular structures. Our approach consists of a randomized perturbation of the converged electron density (matrix) intended to push SCF convergence to orbitals that correspond to another stationary point (of potentially lower electronic energy) in the variational parameter space of an electronic wave function approximation.

I. INTRODUCTION

The rapid increase of computational power and the appearance of new technologies in the last decades have been a driving force in the development of algorithms in quantum chemistry. This has facilitated the development of novel approaches such as real-time quantum chemistry, the interactive optimization of molecular structures,\textsuperscript{6} \textit{ab initio} molecular dynamics,\textsuperscript{7} the interactive combination of atomistic simulations and art,\textsuperscript{8,9} new approaches to the visualization of quantum mechanical data,\textsuperscript{10} and the introduction of computer games in the related field of quantum physics.\textsuperscript{11,12}

Underlying real-time quantum chemistry\textsuperscript{3,5} is the ultra-fast quantum chemical calculation of molecular quantities in such a way that they can be analyzed instantaneously. We developed a computer program that allows one to interact with molecules during a quantum chemical exploration of sequences of molecular structures.\textsuperscript{5,13–15} Our program displays a three-dimensional visualization of a molecular system whose energy, gradients, and other properties are calculated continuously from first principles. An operator can manipulate the molecular system by moving atoms or groups of atoms and will be able to immediately experience the effect of this manipulation on the molecular system. In particular, our program can be coupled to a force-feedback haptic device that allows the operator to move atoms in three dimensions and instantaneously feel the force on these atoms brought about by the structure distortion. The immediate (haptic and visual) feedback provides intuitive insights into the physics and chemistry of the molecular system under study. We detected in some real-time reactivity explorations, molecular behavior that contradicted chemical knowledge (see below for examples) and that could be traced back to wrongly converged quantum chemical calculations. The problem can be attributed to the existence of multiple self-consistent field (SCF) solutions in Hartree–Fock and Kohn–Sham density-functional theory (DFT) calculations. Both theories require the solution of the Roothaan–Hall equations, which can be fulfilled by different self-consistent electronic densities \textit{for the same state and structure}. While some solutions are unstable, others correspond to different energy minima in the space of the molecular orbital coefficients, of which in general only the global minimum corresponds to the desired SCF solution. Nevertheless, the integrity of such calculations is rarely verified, since usually the desired solution is obtained. However, convergence to different SCF solutions is more common than expected. It may occur and remain undetected in ordinary quantum chemical calculations.

It is of utmost importance to ensure correct convergence of SCF calculations, especially in \textit{ab initio} molecular dynamics,\textsuperscript{16} in interactive\textsuperscript{4,5} or automated\textsuperscript{17–23} explorations of chemical reactivity, and in high-throughput screening calculations, where results can hardly be manually validated. Section II describes the origin and consequences of multiple SCF solutions in Hartree–Fock and Kohn–Sham DFT theory. Then, Section III puts this in the context of simulations involving consecutive electronic structure calculations for different geometries of a molecular system and illustrates the problem with

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some examples from real-time reactivity explorations. Section IV introduces a strategy to solve the problem and presents our implementation in a real-time quantum chemistry framework. Then, in Sections V and VI, we apply the approach proposed in different real-time reactivity explorations and in standard quantum chemical calculations.

II. MULTIPLE SCF SOLUTIONS IN HARTREE–FOCK AND KOHN–SHAM DFT THEORIES

In Hartree–Fock and Kohn–Sham DFT theories, one seeks to obtain the molecular orbitals that minimize the total energy (variational principle). To find this energy minimum, one usually sets the condition of stationarity upon changes in the molecular orbitals, which delivers a set of non-linear equations. These equations are a necessary, but not a sufficient condition to obtain the global energy minimum: one may obtain some solution which is a stationary point not necessarily the global or even a local energy minimum of the energy functional.

The central step underlying Hartree–Fock and Kohn–Sham DFT calculations is the iterative solution of the non-linear Roothaan–Hall equations,

\[
FC = SC\varepsilon, \tag{1}
\]

with the Fock matrix \(F = F(C)\), the matrix of the molecular orbital coefficients \(C\), the overlap matrix \(S\), and the diagonal matrix \(\varepsilon\) containing the single-particle energies. The molecular orbitals characterized by \(C\) are updated in every SCF iteration step, and the occupied ones enter the calculation of the electronic density or density matrix according to the Aufbau principle. The electronic density (matrix) then defines the Fock matrix for the next iteration. Unless degenerate orbitals are not equally occupied, the electronic density obtained at any iteration step is well defined. However, the result of the whole SCF procedure depends on the initial Fock matrix (more precisely, on the molecular orbitals with which it is built) as well as on the convergence algorithm.

We emphasize that the multiple self-consistent solutions discussed here all fulfill the Aufbau principle and correspond to the same molecular structure and electronic state characterized by some global quantum numbers. They may, however, correspond to different electronic energies. For exact DFT, convergence to the correct ground-state density can be guaranteed for the exact ensemble functional.

Note that we not only address unstable solutions (solutions that do not correspond to minima of the energy functional): we also consider that different SCF solutions may correspond to minima of the energy functional, of which the lowest one is of interest.

While different SCF solutions are characterized by different energies, a Hartree–Fock or Kohn–Sham DFT energy should be unique. To avoid ambiguities in the calculation of Hartree-Fock or Kohn–Sham DFT energies, only one SCF solution can be the correct one (except for degenerate solutions). One is generally interested in the solution that delivers the lowest electronic energy, which is sometimes called the global or absolute minimum, or Hartree–Fock ground state. Here, we will call it global minimum. Usually, the established quantum chemical algorithms find this solution directly.

In quantum chemical calculations, the choice of quantum numbers and symmetries determines which solutions are obtained, but the fundamental problem of multiple SCF solutions will remain. For example, multiple local minima have been reported for closed-shell Hartree–Fock calculations and Perdew–Zunger self-interaction corrected DFT calculations relying on complex orbitals. In the following, the discussion and calculations refer to unrestricted calculations, but our results have analogous implications for restricted calculations or for calculations with complex orbitals. It can be argued whether and when applying the spin-unrestricted formalism and choosing one of its solutions allows for an adequate description of the electronic wave function. Nevertheless, especially in Kohn–Sham DFT studies, one usually relies on such wave functions although for a single-determinant approximation a symmetry must be broken (total spin or particle number) in order to deal with certain static correlation cases. Furthermore, unrestricted orbitals even allow for compact expansions of full configuration interaction calculations.

III. SERIES OF SIMILAR MOLECULAR STRUCTURES

A. Multiple SCF solutions for consecutive calculations of similar molecular structures

In real-time quantum chemistry, \textit{ab initio} molecular dynamics, and geometry optimizations, electronic structure calculations are executed for many consecutive molecular structures. In general, the electronic densities for two consecutive structures are very similar, since the coordinates of the atomic nuclei change only moderately between two single-point calculations. As a consequence, a converged density matrix is an adequate guess for the next step, which also reduces computational time considerably. This can further be improved by extrapolation techniques.\(^{14,51,52}\)

Along a reaction path, however, there may be discontinuities or bifurcations with respect to the correct SCF solution. At such points, the previous density matrix is not an adequate guess and may lead to convergence to some local-minimum SCF solution. In such cases, wrong
quantum chemical properties are obtained (especially, incorrect nuclear forces), which in turn steer the whole process into a wrong direction.

B. Examples of incorrect convergence for contiguous sequences of structures

In the following, we illustrate for simple examples how, in a sequence of molecular structures, quantum chemical results, which are initially correct, lead to incorrect chemical behavior. In the first three examples, the electronic density is caught in an initially correct restricted solution (in an unrestricted framework). The fourth example shows that undesired convergence can also occur in open-shell cases with odd numbers of electrons. The sequences of structures of this section were generated by real-time manipulation of molecules in our real-time quantum chemistry framework.\textsuperscript{5,13–15} Note that sequences generated in automated calculations (such as structure optimizations) or in molecular dynamics simulations could also bring about similarly incorrect behavior.

In a real-time setting, odd chemical behavior is easily detectable by experiencing unexpected atomic forces when operating a haptic device or by observing unexpected bond orders (calculated, for instance, according to Mayer\textsuperscript{53} and indicated in the visualization by an automatically adjusted width of the sticks indicating chemical bonds).

All energies and forces reported for the following examples were obtained from unrestricted calculations with the PM6 method.\textsuperscript{54} The one-dimensional exploration coordinate in all figures below that report PM6 calculations is given without units. However, we note that the numbers assigned to the exploration coordinate in these figures actually denote seconds and correspond to the time required for the real-time exploration. The explicit Cartesian coordinates along such a collective coordinate are provided in the Supporting Information.

1. Hydrogen abstraction in CH\textsubscript{4}

A well-known example for undesired SCF convergence is the hydrogen abstraction in methane (Fig. 1). In the equilibrium geometry, the correct SCF solution is of (spin-)restricted character. Upon dissociation of one of the hydrogen atoms, the system remains in a restricted solution, even when the underlying calculation is based on the unrestricted formalism. A spin-symmetry breaking in an unrestricted calculation can eventually produce the lowest-energy H + CH\textsubscript{3} dissociation channel in a single-determinant framework, but it can be necessary to enforce this as otherwise the restricted (electron-pairing) solution may prevail.

In a real-time exploration of this hydrogen abstraction reaction with a haptic device, the operator will feel a strong attraction towards the carbon atom even after pulling the hydrogen atom to a considerable distance. Furthermore, the visualization points to wrong orbital convergence as a bond is drawn because of a Mayer bond order close to one between the abstracted hydrogen atom and the carbon atom (Fig. 1), whereas none would be expected.

![Correct SCF convergence: Incorrect SCF convergence:](image)

**FIG. 1.** Abstraction of a hydrogen atom in methane. Top: Correct, expected behavior. Bottom: Incorrect behavior realized when no special care is taken regarding SCF convergence and flagged by a non-vanishing Mayer bond order between the abstracted hydrogen atom and the carbon atom (indicated by a stick representing the bond). Hydrogen and carbon atoms are depicted in white and black, respectively.

2. Hydrogen atom manipulation in ethane

In a real-time manipulation of one of the hydrogen atoms of ethane, transferring it from one side of the molecule to the other may result in artificial atomic forces (repulsion from the carbon atom) and eventually in dihydrogen dissociation, instead of regenerating an ethane molecule in a different conformation. This is illustrated in Fig. 2.

3. Rotation around the double bond of ethene

Fig. 3 shows energy profiles for a rotation around the double bond of ethene. One expects to obtain an energy minimum for angles of 0, 180, and 360 degrees, which correspond to identical structures, as well as an energy maximum for angles of 90 and 270 degrees. However, consecutive calculation of the structures in the sequence may deliver an incorrect energy profile with an energy maximum at 180 degrees.
Correct SCF convergence:

Incorrect SCF convergence:

FIG. 2. Abstraction and re-binding of a hydrogen atom in ethane. Top: Correct behavior. Bottom: Incorrect behavior, realized when no special care is taken regarding SCF convergence. Hydrogen and carbon atoms are depicted in white and black, respectively.

FIG. 3. PM6 energy profiles for the rotation around the double bond of ethene. The incorrect profile is obtained when no special care is taken regarding SCF convergence and each converged electronic density is a guess for the next molecular structure. Hydrogen and carbon atoms are depicted in white and black, respectively.

4. Radical polymerization of ethene

The next example considers ethene polymerization starting from a methyl radical (Fig. 4). In a real-time exploration of this reaction, it is sometimes not possible to make the ethene molecule react with the polymer radical by moving it towards the growing chain with the haptic device (Fig. 5): one experiences a repulsive force, and the radical end of the polymer moves away.

FIG. 4. Model reaction for ethene polymerization.

FIG. 5. Cumbersome step during an interactive exploration of the radical polymerization of ethene. The carbon atom depicted in red is moved towards the radical end of the chain with a haptic device, but the radical end moves out of the way and no reaction occurs. Hydrogen and carbon atoms are depicted in white and black, respectively.

IV. ENFORCING SCF CONVERGENCE TO LOWEST-ENERGY SOLUTIONS

A. General considerations

Many strategies exist to enable or improve SCF convergence into a self-consistent solution (see, for example, Ref. 55 and references cited therein). However, as already observed more than 30 years ago, “computational efforts are usually concentrated on convergence alone, and a solution that has converged in both the energy and density matrix is usually accepted as the ‘true’ solution, within the given approximations". It is seldom verified that the true solution (global SCF minimum) is obtained and not an unstable solution (such as a saddle point) or another local minimum. Compared to the issue of convergence alone, little work has been done about locating the global SCF minimum.

Unstable SCF solutions can be detected by stability analyses. A stability analysis consists in calculating the lowest eigenvalue of the electronic Hessian, which will be negative for an unstable solution. Stability analysis is a very useful tool to verify that the obtained SCF solutions are minima of the energy functional and not just saddle points. Although stability analyses can be applied to any Hartree–Fock or Kohn–Sham wave function, it is usually only applied to avoid getting stuck in a closed-shell solution. Accordingly, stability analyses often search for singlet and triplet instabilities. In comparison, unstable broken-symmetry solutions are rarely discussed. Stability-analysis calculations are commonly not applied because of the relatively high computational cost neces-
sary for the construction of the electronic Hessian. Furthermore, stability analyses cannot distinguish between local and global minima.

To be certain that a SCF solution is the correct one, little can be done but to ensure that there exists no other self-consistent solutions with lower energy. For this, one needs to explore thoroughly the space of possible electronic densities (density matrices), as in SCF metadynamics or in simulated annealing approaches.

In real-time quantum chemistry, convergence to non-global minima must be detected automatically and as rapidly as possible. While only exhaustive search can ensure that the correct SCF solution has been found, this is impractical except for very small systems: the high dimensionality of the parameter space in which the solution must be found implies unaffordable computational cost for ultra-fast or big-data applications.

In the following, we present a solution for real-time quantum chemistry that is satisfactory in terms of speed and efficacy. Afterwards, we discuss how to modify it for single-point calculations and ab initio molecular dynamics.

B. Strategy for real-time quantum chemistry

Smoothness in real-time reactivity explorations is achieved by frequent delivery of nuclear forces. In order to preserve this smoothness, the solution presented here involves no change in the calculations delivering the energies and forces underlying the exploration. Instead, our approach consists in launching, in the background, frequent additional single-point calculations that attempt to find a lower energy for the last electronic structure calculation executed in the reactivity exploration. Each of these calculations starts from a different electronic density (matrix) guess, and will converge either to the same SCF solution or to another one of higher or lower energy.

This guess for the additional calculation is obtained by perturbing the converged molecular orbitals of the reference single-point calculation. The aim is to sufficiently modify the guess electronic structure in order to steer the SCF calculation into different self-consistent solutions. It is important to randomize this perturbation. Randomizing it allows us to explore consecutively different regions of the molecular orbital space and therefore increases the chance of reaching the basin leading to the global minimum if this solution is different from the one already found. Furthermore, without randomization the perturbation would always deliver similar guesses, which is not optimal.

We implement the perturbation by randomly selecting multiple pairs of occupied–unoccupied molecular orbitals and randomly mixing them. We found that the selection of ten pairs works very well for all cases studied here, but this may, of course, be changed on input. As our perturbation calculations are carried out for contiguous sequences of molecular structures, we found that it is not necessary to perturb every structure and that one such perturbation calculation per structure is sufficient, as a different (randomly) perturbed guess will be tried for a similar structure shortly after the last perturbation calculation. Clearly, for individual structures one may inspect more than one perturbed guess at a time.

Our perturbation approach can be compared to the one applied in the SCF metadynamics implementation of Q-Chem, and we note that other perturbation schemes are also possible. By contrast, electron smearing (see, e.g., Refs.) allows for a fractional occupation of orbitals and is usually applied for orbitals that are difficult to converge because of close lying frontier orbitals. In general, however, it does not help to detect incorrect SCF convergence. Our approach, however, introduces more drastic changes to the guess orbitals in order to drive convergence to other minima in parameter space if possible.

If a perturbation calculation finds the same SCF solution or one with a higher energy, it will be ignored. However, if a SCF solution with a lower energy is obtained, the corresponding molecular orbitals will be injected into the reactivity exploration as a guess density matrix for the next single-point calculation. The injection of another electronic density introduces a discontinuity in observables assigned to the sequence of structures. For ultra-fast calculations, this may be acceptable, but it can be avoided by resetting the calculation to previous structures of the reactivity exploration.

This strategy is illustrated schematically in Fig. 6. It cannot guarantee that an incorrect SCF convergence will be detected immediately. However, in a real-time setting the additional calculations are very fast, so that they can be performed frequently without hampering the reactivity exploration. In case of incorrect convergence, this strategy will end up finding the correct solution with a high probability. In general, the many verifications, each of which starts from different electronic densities, ensure that this happens very rapidly (see Section V for examples).

C. Implementation

We implemented approach was implemented in our real-time framework, which is interfaced to the SAMSON molecule viewer.

For the perturbation of the molecular orbitals, our current scheme selects randomly, out of the 15 highest occupied and the 15 lowest unoccupied molecular orbitals,
D. Single-point calculations, structure optimizations, and \textit{ab initio} molecular dynamics

The orbital perturbation introduced here to detect and eventually avoid undesired orbital convergence can also be beneficial in single-point calculations, structure optimizations, and \textit{ab initio} molecular dynamics. For single-point calculations, a computer program can, after converging a set of orbitals, launch one or several calculations after perturbation of the converged molecular orbitals (MO) as discussed above. It can then automatically inspect whether a solution with lower energy is found. While this cannot ensure that the solution is the global minimum, it is an inexpensive, efficient, and reliable test as will be seen in the examples below. Such a test is complementary to standard stability analysis and increases the confidence that a SCF solution is neither a saddle point nor a non-global minimum. For \textit{ab initio} molecular dynamics, the orbital perturbations can be executed every few steps of a simulation trajectory. The same is possible for structure optimizations. Should an incorrect convergence be detected, the calculations can be rewound to the point where the bifurcation occurred. Although this will increase the computation time, it will be worth the effort and probably unavoidable if simple manual inspection is not possible (e.g., in cases of a vast number of calculations or for complex chemical processes for which one does not have any expectations or prior understanding).
V. EXAMPLES

The approach presented in Section IV solves the incorrect behavior in all examples of Section III B. Out of these examples we describe the polymerization reaction in detail below. In addition, two examples are presented for which it is not trivial to spot insufficient SCF convergence during a reactivity exploration.

For all examples, the energies were obtained with the PM6 method.\textsuperscript{54} The interested reader can find videos for the real-time explorations of the six examples of Section III B and of this Section on the internet.\textsuperscript{72} Below, the profiles obtained with and without convergence verification are compared. The corresponding coordinate files can be found in the Supporting Information. In all cases where we observed a bifurcation of energy profiles due to our orbital perturbation approach this was detected almost instantaneously so that the exploration required no rewinding to previous structures.

A. Ethene polymerization

When exploring the radical polymerization of ethene starting from the methyl radical (discussed in Section III B) with convergence verification as described above, the reaction can be reproduced as expected.

Fig. 7 shows the energy profile for the recorded trajectory with and without convergence verification. When adding the fifth ethene molecule, the profile without convergence verification starts to depart from the one obtained by our orbital perturbation calculations.

B. Corey–Chaykovsky epoxidation

In a previous work on molecular propensity,\textsuperscript{15} we studied the Corey–Chaykovsky epoxidation shown in Fig. 8 in our real-time quantum chemistry framework.

For the reaction path taken there, the energy profile will run into a wrong SCF solution if no special care is taken, as shown in Fig. 9. As the spin symmetry of the incorrect profile is already broken here, the origin for the incorrect convergence is not triplet instability. We note that we were already aware of the convergence issue in our previous work\textsuperscript{15} and the energies reported there are correct.

C. Oxidation of hydrogen by the iron oxide cation

The reaction path for
\[ \text{FeO}^+ + \text{H}_2 \rightarrow \text{Fe}^+ + \text{H}_2\text{O} \]

is also taken from our work on molecular propensity.\textsuperscript{15} For this reaction, both the lowest-lying sextet and quartet spin states are of interest. When no special care is taken with regard to convergence, the sextet profile is correct (as one might have expected), but in the quartet state the calculations run into an incorrect SCF solution (Fig. 10). We note again that the results reported in Ref. 15 show the correct convergence behavior and that our perturbation approach solves the problem automatically.

VI. COMPARISON WITH STANDARD DFT CALCULATIONS

To show that the severe convergence issues discussed in this paper are a general problem for computational chemistry not limited to semi-empirical methods, two of the examples considered above were studied with standard DFT methods (PBE0\textsuperscript{73}, def2-TZVP\textsuperscript{74}), for which we applied the program TURBOMOLE\textsuperscript{75} (version 6.5). We chose this program for its very stable and reliable con-
FIG. 9. Electronic PM6 energies for the Corey–Chaykovsky epoxidation. The peak around coordinate 11.5 appeared when the operator chose to change the position of the carbon atom to carry out the second part of the reaction.

FIG. 10. Electronic PM6 energies for the oxidation of hydrogen by the iron oxide cation (lowest quartet spin state). The second incorrect profile was obtained when resetting the correct molecular orbitals at the intermediate.

For both examples, we calculated three energy profiles. First, for each structure, we calculated the energies delivered when starting the calculation from an Extended-Hückel Theory (EHT) guess. Second, we calculated an energy profile where the starting orbitals for each structure are taken from the converged orbitals of the previous structure. Finally, we added a perturbation of the molecular orbitals for every fifth structure and injected the corresponding molecular orbitals if the calculation had delivered a lower energy. For this, we wrote a utility program that transforms the molecular orbitals delivered by TURBOMOLE according to the algorithm presented in Section IV C. In all calculations we applied the standard TURBOMOLE settings, in particular a total electronic energy convergence criterion of $10^{-6}$, unless otherwise noted.

A. Rotation around the double bond of ethene

The DFT energies obtained for the rotation around the double bond of ethene are illustrated in Fig. 11.

FIG. 11. Electronic PBE0/def2-TZVP energies for rotation around the double bond of ethene. The trajectory consists of 361 structures. The perturbed energy profile is obtained by perturbing the molecular orbitals every fifth structure.

Here, both the EHT guess and the normal propagation of the molecular orbitals deliver wrong energies for structures around angles of 90 and 270 degrees. The energies obtained with the EHT guess reflect the restricted solution, and normal propagation of the orbitals runs into another restricted solution for angles slightly larger than 90 and 270 degrees, before finding the correct, unrestricted solution. With the perturbation of the molecular orbitals, the simulation switches rapidly to the correct solution.
The three SCF solutions obtained at an angle of 102 degrees were analyzed in detail, and a table summarizing their differences is available in the Supporting Information. There, isosurfaces for the highest occupied and lowest unoccupied molecular orbitals show that their electronic structure is considerably different. For instance, the order of the orbitals in the two closed-shell solutions is different (although the Aufbau principle is fulfilled in both cases). Stability analysis of the (unrestricted) SCF solutions obtained with the EHT guess or without perturbation reveals a triplet instability. Recalculation of these unstable solutions in the restricted formalism and subsequent stability analysis of the closed-shell solutions show that they are local minima in the restricted formalism (i.e., they have no singlet instability).

Interestingly, for the structure with an angle of 90 degrees, employing the triplet molecular orbitals as a guess for the singlet calculation still produces the same incorrect solution. In this case, setting a tighter convergence threshold for the total electronic energy \(10^{-9}\) is necessary to find the correct solution after thousands of SCF iterations.

**B. Oxidation of hydrogen by the iron oxide cation**

The three energy profiles obtained for the sextet state of the oxidation of hydrogen by the iron oxide cation are identical and will not be shown here. However, for the quartet state, they all differ as can be seen in Fig. 12 (the Supporting Information contains enlarged figures for the sake of clarity).

The three energy profiles deviate little, but various observations can be made. First, the energies obtained in this example confirm the existence of different SCF solutions. Especially, we see that the solution resulting from the EHT guess is sometimes considerably different from the lowest-energy solution obtained here. Second, the energies of the propagated profile are largely correct, but sometimes correspond to a non-global minimum and slightly differ in the energy (for instance at coordinates around 3.8, 8.5, 9.5 and 12.5, see Supporting Information). Third, the perturbed profile does not always deliver the lowest energy either. However, the perturbations allow for detecting this early, and, as a whole, the perturbed profile is better than both other profiles in this case.

A more detailed analysis reveals both stable and unstable incorrect SCF solutions. For instance, at coordinate 25.5, three different energies are delivered by the three calculations. While a stability analysis for the solution obtained from the EHT guess detects an instability (negative eigenvalue in the electronic Hessian), the other two solutions are stable. After enforcing convergence of the unstable solution into a minimum, a fourth SCF solution is found, three of which are distinct, non-degenerate local SCF minima. The Supporting Information contains a table summarizing the properties of these four SCF solutions. Whereas some of them are characterized by qualitatively different molecular orbitals, others seem to be similar. In the case of the latter, also the total electronic energies of the three local SCF minima are very similar. Still, they represent different solutions as it is not possible to converge them to one solution by enforcing the convergence thresholds. Note that the kinetic and potential energy contributions of these solutions with similar energies are notably different.

**VII. CONCLUSIONS**

Many quantum chemical studies rely on Hartree–Fock and Kohn–Sham DFT theories. An unpleasant feature of these theories is that they allow for multiple solutions. In general, only one of them is of interest: the solution yielding the lowest electronic energy. Usually, the established quantum chemical algorithms find the correct solution directly. There, however, cases in which SCF calculations find the correct electronic ground-state density and some other self-consistent solution is found.

When the quantum chemical calculations find incorrect SCF solutions, the calculated properties are unreliable. In real-time quantum chemistry, incorrect SCF convergence can sometimes be spotted easily, for instance, by...
experiencing highly artificial force feedback or because bonds are displayed where none is expected.

This problem cannot be solved trivially and so no simple and universal solution exists. In particular, stability analysis will only be able to detect unstable self-consistent solutions of the energy functional (such as saddle points), but cannot provide information on whether a solution corresponds to a local or to the global minimum.

To avoid incorrect behavior and ensure the reliability of real-time reactivity explorations, the strategy adopted in this work is to continuously search, in the background, for a better SCF solution than the one currently delivering energy and forces underlying a simulation. With drastic random perturbations of the molecular orbitals, these background convergence verifications detected incorrect SCF convergence very rapidly. While our approach cannot guarantee with certainty that incorrect SCF convergence will be detected, we have discovered no case where it failed and it has become a vital component of our real-time quantum chemistry framework.

Since single-point calculations, structure optimizations, and \textit{ab initio} molecular dynamics can also suffer from incorrect SCF convergence, we discussed variants of our approach that can be beneficial in these settings. From the examples shown in this work, it is evident that convergence to undesired solutions, be it saddle points or non-global minima of the energy functional, are more common than expected. The potential benefit of applying the approach presented in this work outweighs its extra computational cost, even in case of expensive SCF calculations. In \textit{ab initio} molecular dynamics simulations and structure optimizations, such verifications are not necessary at every time or structure step so that the additional cost are manageable.

Whereas this work focused on single-reference methods, similar convergence issue may arise in multi-configuration SCF (MC-SCF) calculations. MC-SCF methods also rely on non-linear equations and hence MC-SCF solutions can, in principle, be caught in local minima.\textsuperscript{32}

\section*{ACKNOWLEDGMENTS}

The authors gratefully acknowledge support by ETH Zurich (grant number: ETH-20 15-1).

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\textsuperscript{24}J. Hachmann, R. Olives-Amaya, S. Atahan-Evrenk, C. Amador-Bedolla, R. S. Sanchez-Carrera, A. Gold-Parker, and J. K. precise random perturbations of the molecular orbitals, these background convergence verifications detected incorrect SCF convergence very rapidly. While our approach cannot guarantee with certainty that incorrect SCF convergence will be detected, we have discovered no case where it failed and it has become a vital component of our real-time quantum chemistry framework.

Since single-point calculations, structure optimizations, and \textit{ab initio} molecular dynamics can also suffer from incorrect SCF convergence, we discussed variants of our approach that can be beneficial in these settings. From the examples shown in this work, it is evident that convergence to undesired solutions, be it saddle points or non-global minima of the energy functional, are more common than expected. The potential benefit of applying the approach presented in this work outweighs its extra computational cost, even in case of expensive SCF calculations. In \textit{ab initio} molecular dynamics simulations and structure optimizations, such verifications are not necessary at every time or structure step so that the additional cost are manageable.

Whereas this work focused on single-reference methods, similar convergence issue may arise in multi-configuration SCF (MC-SCF) calculations. MC-SCF methods also rely on non-linear equations and hence MC-SCF solutions can, in principle, be caught in local minima.\textsuperscript{32}

\section*{ACKNOWLEDGMENTS}

The authors gratefully acknowledge support by ETH Zurich (grant number: ETH-20 15-1).

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