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*J. Chem. Phys.* 142, 154109 (2015)  
<https://doi.org/10.1063/1.4918561>

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# Stability of the complex generalized Hartree-Fock equations

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(Received 19 December 2014; accepted 2 April 2015; published online 16 April 2015)

For molecules with complex and competing magnetic interactions, it is often the case that the lowest energy Hartree-Fock solution may only be obtained by removing the spin and time-reversal symmetry constraints of the exact non-relativistic Hamiltonian. To do so results in the complex generalized Hartree-Fock (GHF) method. However, with the loss of variational constraints comes the greater possibility of converging to higher energy minima. Here, we report the implementation of stability test of the complex GHF equations, along with an orbital update scheme should an instability be found. We apply the methodology to finding the local minima of several spin-frustrated hydrogen rings, as well as the non-collinear molecular magnet Cr<sub>3</sub>, illustrating the utility of the broken symmetry GHF method and some of its lesser-known nuances. © 2015 AIP Publishing LLC. [<http://dx.doi.org/10.1063/1.4918561>]

## I. INTRODUCTION

It has been known for a while that requiring approximate, variational Hamiltonians to have the same symmetries as the exact Hamiltonian adds additional constraints to the variational problem.<sup>1–5</sup> Such constraints can only raise the energy, contrary to the goal of the variational method. As first pointed out by Löwdin,<sup>6</sup> the practicing quantum chemist is faced with a dilemma: should one seek an approximate solution that is a true variational minimum, or should one seek solutions that retain the correct symmetry of the exact solution? For approximate Hartree-Fock solutions, one cannot have both simultaneously. Insisting that we abandon symmetry constraints, we recover the generalized Hartree-Fock equations (GHF). GHF is a non-collinear method, meaning that spin-orbitals are allowed to exist in a superposition of spin-up and spin-down states. This allows each spin quantization axis to rotate freely, which is necessary for systems with complex and competing magnetic interactions, such as geometrically frustrated systems. GHF and non-collinear approaches will be necessary for their description.<sup>7–14</sup> For example, taking the advantage of the flexibility in the spin degrees of freedom, we have recently applied the time-dependent formalism of GHF to *ab-initio* non-relativistic spin dynamics.<sup>15</sup>

The complex GHF method is part of a family of broken symmetry methods in the independent particle model. The broken symmetry methods were first mapped out by Fukutome,<sup>2</sup> and later clarified and renamed by Stuber and Paldus.<sup>3</sup> The real-valued unrestricted Hartree-Fock (UHF) method, for example, is the name of the Hartree-Fock method that breaks  $\hat{S}^2$  symmetry but is invariant to complex conjugation and rotations by  $\hat{S}_z$ . As is well known, UHF solutions are not eigenfunctions of  $\hat{S}^2$ , and this is to be expected from symmetry analysis. A thorough description of broken symmetries in the independent particle model is given by Stuber and Paldus.<sup>3</sup> Invariance to symmetry operations provides good quantum

numbers. Thus, a true GHF solution cannot be classified by any spin quantum numbers. As will be shown later, broken symmetries also imply degeneracies which provide a route to restoration of symmetry (and good spin quantum numbers).<sup>16,17</sup> One such route is to take a linear superposition of broken symmetry solutions. Recently, the projected Hartree-Fock method<sup>18,19</sup> has been proposed and tested as a route to restore symmetry in broken symmetry solutions. In any case, it is crucial to note that such restoration may only be done at the multireference level. We do not concern ourselves with multireference solutions any longer, and explore single-determinant solutions from here on out.

An even more concerning issue arises even at the single-determinantal level. Removing symmetry constraints from the Hartree-Fock model provides the additional degrees of freedom necessary to converge to a true broken symmetry minimum (if one exists). However, with the additional degrees of freedom comes the increased chance of converging not to the true energetic minima, but rather a higher order saddle point. GHF is notorious for converging to higher energy saddle points. By changing the initial GHF guess, one may converge to all sorts of higher order solutions. Thus, when using GHF, it is critical to ensure that the solution obtained is a true local minimum. Furthermore, if the solution is not a true local minima, methods must be devised to reoptimize GHF so that it does converge on the true energetic minimum. Here, we report the derivation and implementation of the stability conditions and orbital rotations necessary to ensure the true GHF minimum is obtained. Having done this, we explore the utility of GHF when it is applied to surprisingly tricky spin-frustrated ring systems.

## II. THEORY

Much work has gone into deriving the general stability conditions for the Hartree-Fock equations, and we briefly derive these conditions following the work of Čížek and Paldus.<sup>20</sup> In the present work, we adopt the notation that indices

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$i, j, k, l$  refer to occupied orbitals,  $a, b, c, d$  refer to virtual orbitals, and  $p, q, r, s$  refer to any orbital. We also adopt Einstein summation, where the summation over common indices is implied. We begin with the Thouless representation of a single determinant. Thouless showed that any single Slater determinant can be transformed into another non-orthogonal single determinant via the transformation<sup>21</sup>

$$|\tilde{\phi}\rangle = e^{\hat{T}_1}|0\rangle, \quad (1)$$

where  $\hat{T}_1$  is a single particle excitation operator

$$\hat{T}_1 = \sum_{ia} t_i^a \{a_a^\dagger a_i\}. \quad (2)$$

In order to ensure that the Thouless transformation is enacted by a unitary transformation, we insist on the condition that  $\hat{T}_1$  is skew-Hermitian, i.e.,

$$\hat{T}_1 = -\hat{T}_1^\dagger \quad (3)$$

which implies that

$$t_i^a = -t_i^{a*}. \quad (4)$$

Consider the connected energy functional

$$E = \langle \tilde{\phi} | \hat{H}_N | \tilde{\phi} \rangle_c = \langle 0 | e^{\hat{T}_1^\dagger} \hat{H}_N e^{\hat{T}_1} | 0 \rangle_c, \quad (5)$$

where

$$\begin{aligned} \hat{H}_N &= \hat{H} - \langle 0 | \hat{H} | 0 \rangle = \hat{F}_N + \hat{V}_N = f_{pq} \{a_p^\dagger a_q\} \\ &\quad + \frac{1}{4} \langle pq || rs \rangle \{a_p^\dagger a_q^\dagger a_s a_r\} \end{aligned} \quad (6)$$

and  $\hat{H}$  is our Hamiltonian.  $\hat{F}_N$  and  $\hat{V}_N$  are the one- and two-body operators; the elements  $f_{pq}$  are the elements of the Fock matrix and  $\langle pq || rs \rangle$  are the antisymmetrized two electron integrals. For this parameterized functional, expanding through second order in  $\hat{T}_1$  gives

$$\begin{aligned} E &= \langle 0 | \hat{H}_N + \hat{T}_1^\dagger \hat{H}_N + \hat{H}_N \hat{T}_1 + \hat{T}_1^\dagger \hat{H}_N \hat{T}_1 + \frac{1}{2} \hat{T}_1^\dagger \hat{T}_1^\dagger \hat{H}_N \\ &\quad + \frac{1}{2} \hat{H}_N \hat{T}_1 \hat{T}_1 | 0 \rangle_c. \end{aligned} \quad (7)$$

Taking the first variation of  $E$  with respect to the Thouless parameters  $q_i^a = (t_i^a, t_i^{a*})$  about  $\hat{T}_1 = \hat{T}_1^\dagger = 0$ , gives

$$\frac{\partial E}{\partial q_i^a} = \begin{pmatrix} \langle \phi_i^a | \hat{H}_N | 0 \rangle_c \\ \langle 0 | \hat{H}_N | \phi_i^a \rangle_c \end{pmatrix} = \begin{pmatrix} f_{ai} \\ f_{ia} \end{pmatrix} \quad (8)$$

which must equal zero if the energy functional is minimized. Thus,  $f_{ia} = 0$  which are the off-diagonal elements of the Fock matrix, which is Brillouin's theorem. Taking the second variation of  $E$  with respect to the Thouless parameters yields

$$\frac{\partial^2 E}{\partial q_i^a \partial q_j^b} = \begin{pmatrix} \langle \phi_i^a | \hat{H}_N | \phi_j^b \rangle_c & \langle \phi_{ij}^{ab} | \hat{H}_N | 0 \rangle_c \\ \langle 0 | \hat{H}_N | \phi_{ij}^{ab} \rangle_c & \langle \phi_j^b | \hat{H}_N | \phi_i^a \rangle_c \end{pmatrix}. \quad (9)$$

For the Hartree-Fock equations to be stable, the second variation must be positive semidefinite, i.e.,  $\delta^{(2)}E \geq 0$ . Putting the second variation in matrix form, we obtain the Hessian

$$\begin{pmatrix} \mathbf{A} & \mathbf{B} \\ \mathbf{B}^* & \mathbf{A}^* \end{pmatrix}, \quad (10)$$

where

$$A_{ia,jb} = (\epsilon_a - \epsilon_i) \delta_{ia,jb} + \langle aj || ib \rangle, \quad B_{ia,jb} = \langle ab || ij \rangle. \quad (11)$$

For the complex GHF equations, the orbital energies will be real as they are the eigenvalues of a Hermitian matrix. The antisymmetrized two-electron integrals, however, will be complex. Thus, in the complex GHF case,  $\mathbf{A} \neq \mathbf{A}^*$  and  $\mathbf{B} \neq \mathbf{B}^*$ . At any stationary solution to the Hartree-Fock equations, the above Hessian may be constructed and diagonalized. Strictly negative eigenvalues indicate an instability, and the corresponding eigenvector indicates the direction in which the Hartree-Fock energy will decrease. This can be accomplished by taking the eigenvector corresponding to the lowest eigenvalue (steepest descent) and constructing a complex-valued  $(2N \times 2N)$  mixing matrix  $\mathbf{K}$ , where  $N$  is the number of basis functions,<sup>1</sup>

$$\mathbf{K} = \begin{pmatrix} \mathbf{0} & -\mathbf{J}^\dagger \\ \mathbf{J} & \mathbf{0} \end{pmatrix}, \quad (12)$$

where  $\mathbf{J}$  is the  $(O \times V)$  eigenvector corresponding to the lowest eigenvalue. This mixing matrix is exponentiated to give the unitary rotation matrix that transforms the old set of MO coefficients  $\mathbf{C}$  to a new set of rotated MO coefficients  $\mathbf{C}'$ ,

$$\mathbf{C}' = \mathbf{C} e^{-s\mathbf{K}}, \quad (13)$$

where  $s$  is some small step in the direction  $\mathbf{K}$ . The new rotated MO coefficients may be fed back into the SCF procedure and the Hartree-Fock solutions re-optimized. With a suitable step-size, the Hartree-Fock equations will converge to a lower energy solution, and the stability test may be performed again.

### III. DISCUSSION

Among the first row elements, GHF solutions are rare. However, molecular systems involving geometric frustration are prime targets for a GHF analysis because their frustrated spins must break  $\hat{S}_z$  symmetry in order to minimize Pauli repulsion. Geometrically frustrated systems have long been a target for GHF and noncollinear DFT methods.<sup>7–14</sup> Thus, to explore the applicability of our GHF stability tests, we examined a series of neutral hydrogen rings, ranging from 3 to 15 hydrogens. Each hydrogen was spaced 1 Å around a circle. The advantage of studying such a system is threefold: first, the system is simple enough that we can be guided by chemical intuition, second, at such a spacing, the hydrogen rings act similar to 1D hydrogen chains that prefer an antiferromagnetic alignment, and third, each odd-membered ring will be geometrically frustrated. There are few studies of hydrogen rings,<sup>22,23</sup> but this appears to be the first to study the geometrically frustrated neutral, odd-numbered hydrogen rings. This geometric frustration means that a GHF solution must exist which minimizes the repulsion from the frustrated spin alignment. It bears mentioning that although the system appears to be artificial, equilateral  $H_3^+$  is among one of the most common ions in interstellar gases,<sup>24,25</sup> and  $H_3$  has been observed experimentally.<sup>26</sup> Furthermore, recent combined theoretical/experimental reports have demonstrated the evidence of sigma-aromatic  $H_5^-$  when

complexed with ZnPt.<sup>27</sup> The complex GHF code, stability tests, and orbital update codes were implemented in the development version of Gaussian.<sup>28</sup> All tests were performed using a cc-pvDZ basis,<sup>29</sup> which is the minimum necessary to describe the polarization of hydrogenic s-functions.

Following Blaizot and Ripka,<sup>16</sup> we define a broken symmetry solution as a solution to the approximate Hamiltonian that cannot be classified according to an irreducible representation of the symmetry group of the exact non-relativistic Hamiltonian. In other words, the approximate solution does not carry the quantum numbers of the exact Hamiltonian. For example, while spin projection  $m_s$  is a good quantum number for the exact Hamiltonian, it is not necessarily a good quantum number for the GHF solutions that approximate it.

Qualitatively, the differences between the UHF and GHF solutions are given in Figures 1 and 2, respectively. The magnetization is defined according to the Hirshfeld partitioning given in Refs. 15 and 30. The spin density in the non-collinear approach is a mapping of the 2-norm of the spin magnetization vector<sup>31</sup> onto the total density. This ensures that the spin density is always positive and always real. It is also worth noting that GHF will provide complex density matrices, however, the density matrix is Hermitian and will correspond to a real observable, thus, the total density is real. The charge density is a mapping of the electrostatic potential to the total density. A quantitative energetic comparison is given in Table I. For even numbered rings, GHF and UHF results are identical. Both converge to the same antiferromagnetic

spin distribution, aside from the six and ten membered rings. The six and ten membered rings do not have antiferromagnetic ordering because they are sigma aromatic, following Hückel's  $4j + 2$  rule. This is further evidenced by the large energetic stabilization of these rings relative to the other rings. The fourteen membered ring breaks this pattern however, and shows the beginning of slight antiferromagnetic ordering. In this case, the local ordering of the molecule is moving away from cyclical and towards linear, thus breaking Hückel aromaticity in the large- $n$  case. Although RHF results are not shown, the energetic ordering for even numbered rings goes RHF > UHF = GHF, aside from the aromatic cases. This is understandable, as RHF cannot treat antiferromagnetic ordering.

For odd membered rings, UHF and GHF provide very different solutions. This is the result of geometrical frustration. GHF solutions are always lower energy than the UHF solutions, which is to be expected because it allows for broken-symmetry solutions. The stabilization over UHF ranges from 0.9 kcal mol<sup>-1</sup> for  $n = 3$ , to nearly 10.0 kcal mol<sup>-1</sup> for  $n = 15$ . UHF requires collinear ordering of magnetization, as its solutions are constrained to be eigenfunctions of  $\hat{S}_z$ , and this is clearly seen in the ordering of the magnetization vectors in Figure 2. GHF, on the other hand, has its lowest energy solutions with magnetization vectors arranged in a non-collinear manner. This Möbius-like periodicity of magnetization ordering in GHF results in a totally symmetric distribution of spin density throughout the structure. The distribution of magnetic coupling is maximized in the GHF solutions. On the other

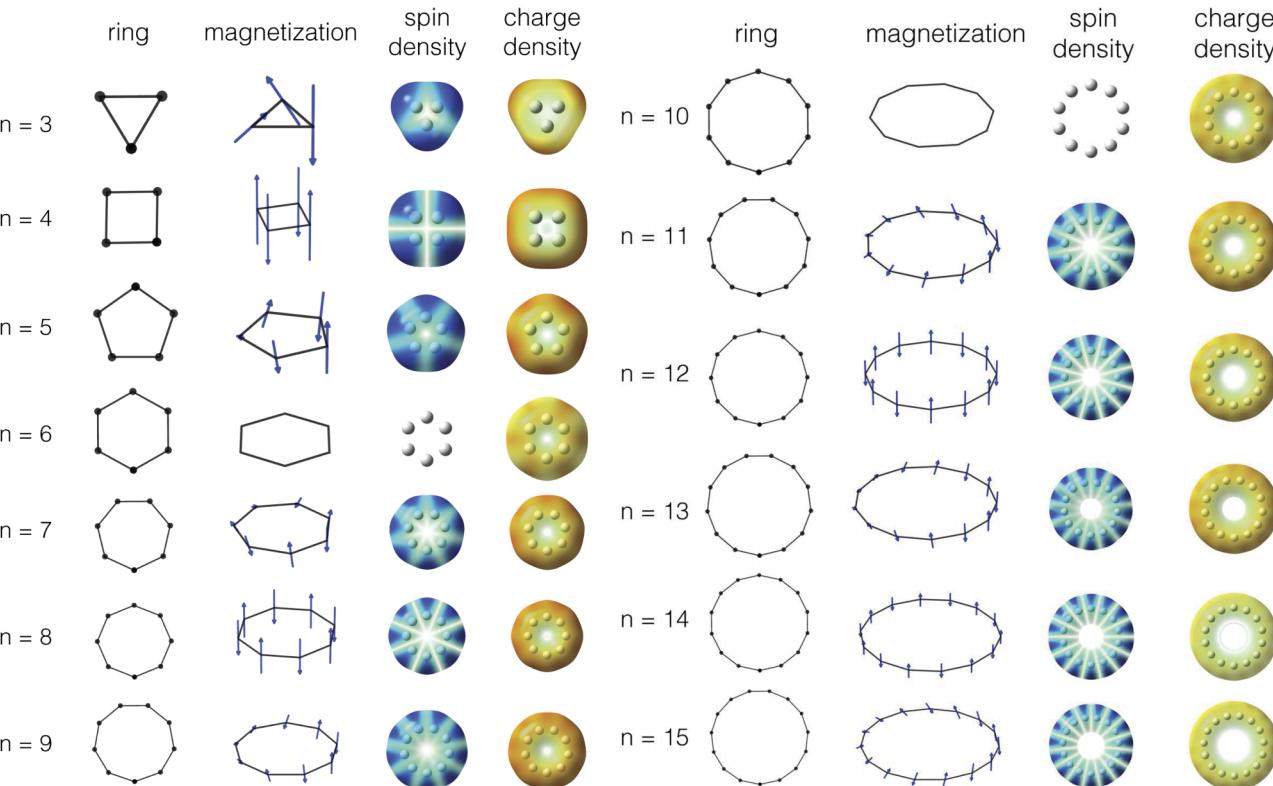


FIG. 1. Local GHF energetic minima of hydrogen rings sizes 3–15. Odd-membered rings break the axial symmetry of the axis normal to the molecular plane; this is unique to GHF solutions and minimizes Pauli repulsion. The spin density is the 2-norm of the magnetization vector at each point in space, with blue being the greatest in magnitude. Charge density is represented as the electrostatic potential mapped to the total density, with red color showing a greater electronic population.

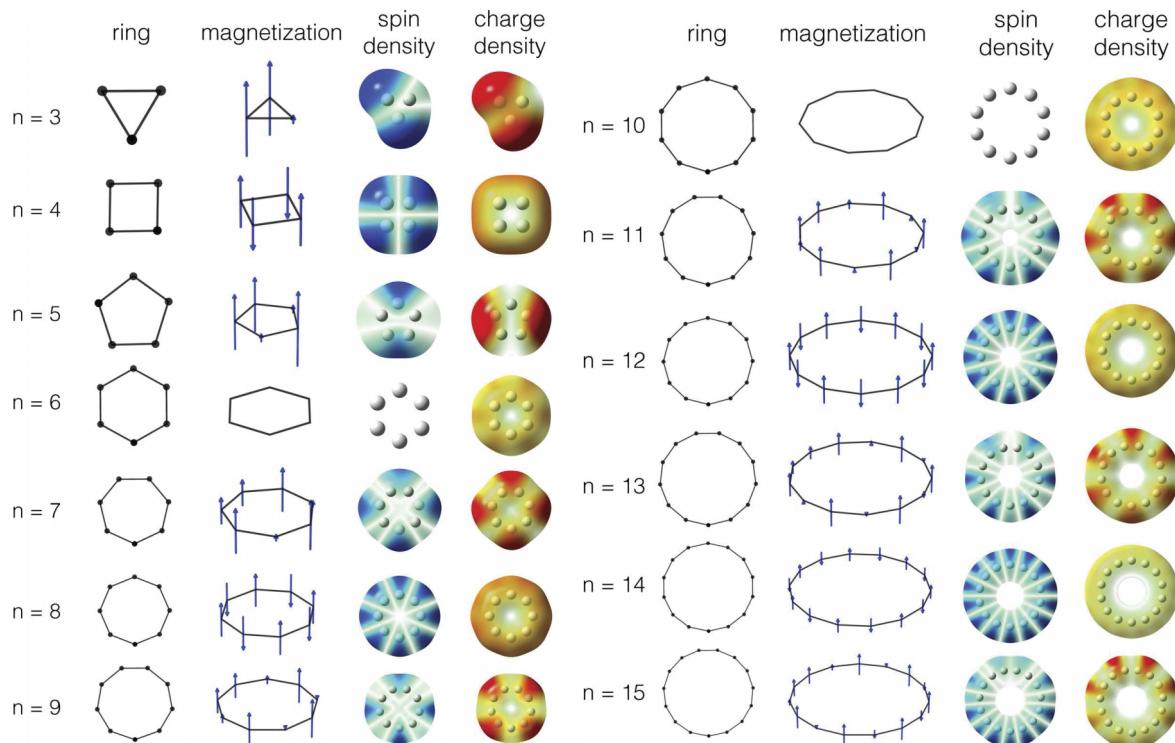


FIG. 2. Local UHF energetic minima of hydrogen rings sizes 3–15. Unlike GHF, the UHF cannot break  $\hat{S}_z$  symmetry (hence collinear magnetizations), resulting in asymmetric spin distribution through the odd-numbered rings. This raises the energy compared to their GHF counterparts. The spin density is the 2-norm of the magnetization vector at each point in space, with blue being the greatest in magnitude. Charge density is represented as the electrostatic potential mapped to the total density, with red color showing a greater electronic population.

TABLE I. Comparison of energetic minima between GHF and UHF for various  $H_n$  rings. Energies are given in kcal mol<sup>-1</sup> from an infinitely separated  $n$ -hydrogen reference. The fourth column gives the difference in energy between GHF and UHF. Energies decrease monotonically except for at  $n = 6$  and  $n = 10$ , corresponding to aromatic stabilization. The far right column gives the number of zeros in the GHF Hessian. All other eigenvalues are positive. For strictly unique GHF solutions, we see three zeros, corresponding to broken symmetry modes along the  $x$ ,  $y$ , and  $z$  spin rotations. When GHF solutions lie on the UHF manifold, we see two zeros, corresponding to broken symmetry modes along the  $x$  and  $y$  spin rotations. When GHF solutions lie on the RHF manifold, as in the  $n = 6$  and  $n = 10$  cases, we see no zeros, corresponding to a fully spin-symmetric solution.

$n$	$\Delta_{\text{GHF}}$	$\Delta_{\text{UHF}}$	$\Delta(\text{GHF-UHF})$	GHF zeros
3	-6.21	-5.30	-0.91	3
4	-15.04	-15.04	0.00	2
5	-59.53	-56.20	-3.33	3
6	-159.35	-159.35	0.00	0
7	-122.34	-118.88	-3.46	3
8	-153.69	-153.69	0.00	2
9	-187.20	-181.79	-5.41	3
10	-251.48	-251.48	0.00	0
11	-236.73	-230.50	-6.23	3
12	-270.94	-270.94	0.00	2
13	-293.98	-286.08	-7.90	3
14	-340.08	-340.08	0.00	2
15	-342.85	-332.63	-10.22	3

hand, UHF solutions must order spins in a lower-symmetry distribution which is especially clear in the  $n = 3$  and  $n = 5$  cases. The charge density further confirms this distribution, with a lower-symmetry charge distribution as a result of

electrons pairing locally instead of delocalizing throughout the ring as in the GHF solutions.

While neither UHF nor GHF is an eigenfunction of  $\hat{S}^2$ , and GHF is not even an eigenfunction of  $\hat{S}_z$ , it is interesting to look at the expectation values of these spin operators, given in Figure 3. GHF has a net zero expected value of  $\hat{S}_z$  for all ring sizes considered, which is characteristic of these broken symmetry solutions. The individual atomic spin magnetizations cancel out. In UHF, such global cancellation of spin magnetization cannot occur in odd-membered rings on account of geometric frustration. The expected value of  $\hat{S}^2$  increases for both GHF and UHF as ring size increases, showing increasing spin contamination in these systems.

While the absence of negative Hessian eigenvalues assures us that the GHF solutions are indeed at a local minimum, we may wonder if the solutions obtained are unique. It turns out that broken symmetry solutions are not unique. In fact, for any broken symmetry, we may find an infinite number of degenerate solutions. This is not difficult to show. Consider a symmetry depending on some real parameter  $\theta$  of the Hamiltonian that satisfies the following:

$$\hat{U}(\theta)\hat{H}\hat{U}(\theta)^\dagger = \hat{H}. \quad (14)$$

Now, consider some GHF solutions that break the above symmetry and are related by the transformation

$$|\phi\theta\rangle = \hat{U}(\theta)|\phi\rangle; \quad |\phi\theta\rangle \neq |\phi\rangle. \quad (15)$$

It then follows that

$$\langle\phi\theta|\hat{H}|\phi\theta\rangle = \langle\phi|\hat{H}|\phi\rangle. \quad (16)$$

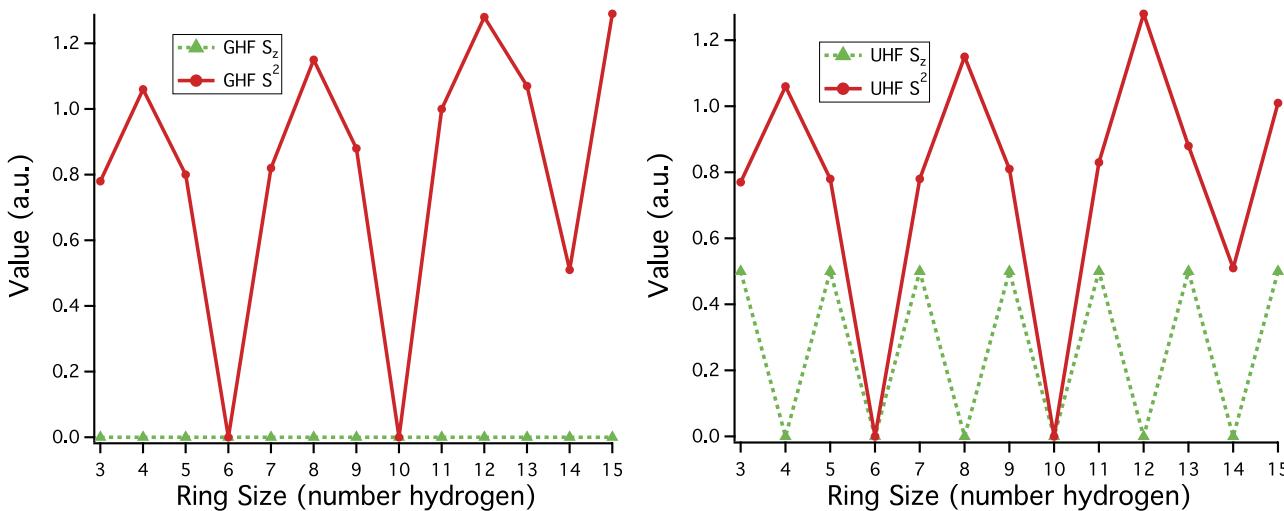


FIG. 3. Expected values of  $\hat{S}_z$  and  $S^2$  operators on GHF (left) and UHF (right) solutions according to ring size. For  $n = 6$  and  $n = 10$ , the solutions converge to a solution on the RHF manifold. These solutions are aromatic, and have a diamagnetic ring current. The anti-aromatic solutions at  $n = 4j$  (where  $j$  is an integer) show the greatest expected value  $\hat{S}^2$ , consistent with a paramagnetic ring current. For odd-membered rings, GHF, unlike UHF, has a zero expected value of  $\hat{S}_z$ , the result of net cancellation of individual spin magnetic moments which is only possible with non-collinear methods.

Which is to say that there degenerate GHF solutions which depend on  $\theta$ , which may be discrete or continuous. Continuously broken symmetries lead to zeros in the Hessian, though the converse is not necessarily true,<sup>16</sup> and many of the implications of broken symmetries in Hartree-Fock have been studied recently.<sup>17</sup> Broken continuous symmetry (which is a manifestation of Goldstone's theorem for finite systems), however, is the origin of the zeros in the GHF Hessian for the hydrogen rings studied. GHF solutions that are uniquely GHF (i.e., impossible to obtain via UHF, etc.) have three zeros in the Hessian. This corresponds to broken spin symmetry modes along the  $x$ ,  $y$ , and  $z$  axes. For GHF solutions that have unique solutions in the UHF manifold, there are two zeros observed in the Hessian, and these correspond to broken spin symmetry modes along the  $x$  and  $y$  axes (meaning  $\hat{S}^2$  is not associated with a good quantum number, but  $\hat{S}_z$  is). For GHF solutions that lie in the RHF manifold, as is the case for  $n = 6$  and  $n = 10$ , there are no zeros; that is, the solutions are invariant to all spin symmetry operations.

Broken symmetry modes can be thought of as collective excitations without a restoring force, and they lead to distinct, degenerate solutions. We can show this empirically by rotating the GHF molecular orbitals in the direction of the zero eigenvalues using our stability updating scheme. Following these eigenmodes will lead us to energetically degenerate and (possibly) distinct solutions to the GHF equations. Following such an approach, we have found several distinct but degenerate solutions for the  $H_3$  and  $H_4$  rings. These are illustrated in Figure 4. The distinct nature of each solutions is most easily seen in the orientation of the magnetization vectors on each atom. Fixing the laboratory reference frame to the top atom in each figure, we see several energetically equivalent magnetization orientations. For  $H_3$ , the atomic magnetizations may point in different directions, some in, some out, some even out of the plane defined by the molecule—all molecular expectation values do not change, but the densities do take on distinct solutions. For  $H_4$  we could only find two degenerate solutions (again, assuming we fix the laboratory reference frame). They

simply alternate spins pointing up and down in equivalent, but distinctly different ways.

This point is important for thinking about the broken symmetry solutions. After all, we know that for a true singlet, the net magnetic moment on each atom must go to zero. The true solution must lie in a superposition between these two solutions, which is a multireference problem. The atomic spin magnetic moments are not static, but dynamic. They fluctuate in a coherent state whose atomic spin moments cancel out to zero. This problem with the GHF solutions was recently identified by Scuseria *et al.*<sup>17,19</sup> and remedied with the projected Hartree-Fock approach. Again, we must mention that this cannot be done at a single determinantal level.

Despite this, complex GHF solutions provide a powerful method to explore the nature of geometric frustration in molecules. Many concepts in magnetic ordering originate in solid-state physics. Just as UHF allows one to take the concepts of (anti)ferromagnetism to the single-molecule domain, so does GHF take the solid-state concept of geometric frustration and apply it to the single-molecule domain. This is important for explorations into local and microscopic origins of exotic magnetic behavior.

As a final demonstration of the utility of the GHF stability equations and update scheme, we apply our methods to the neutral chromium trimer in an equilateral triangle geometry. While this solution is known to have a non-collinear ground state (see, for example, Refs. 7 and 10), reports using unrestricted density functional theory (DFT) predict that neutral  $Cr_3$  has an extremely high spin  $^{17}E$  ground state.<sup>32</sup> We can see how the GHF stability and update scheme connects these two solutions. The solution schematic is given in Figure 5. Following previous work by Sharma *et al.*<sup>7</sup> and Bulik *et al.*,<sup>10</sup> we create a  $D_{3h}$   $Cr_3$  trimer at a bond length of 2.89 Å, close to the high spin  $^{17}E$  ground state unrestricted Kohn-Sham of Papas and Schaefer<sup>32</sup> which had an equilibrium bond length of 2.92 Å. Using a LANL2DZ<sup>33</sup> basis, we find that UHF theory predicts a high spin state as well, though with 18 unpaired electrons instead of 16. This spin state is shown on the left of

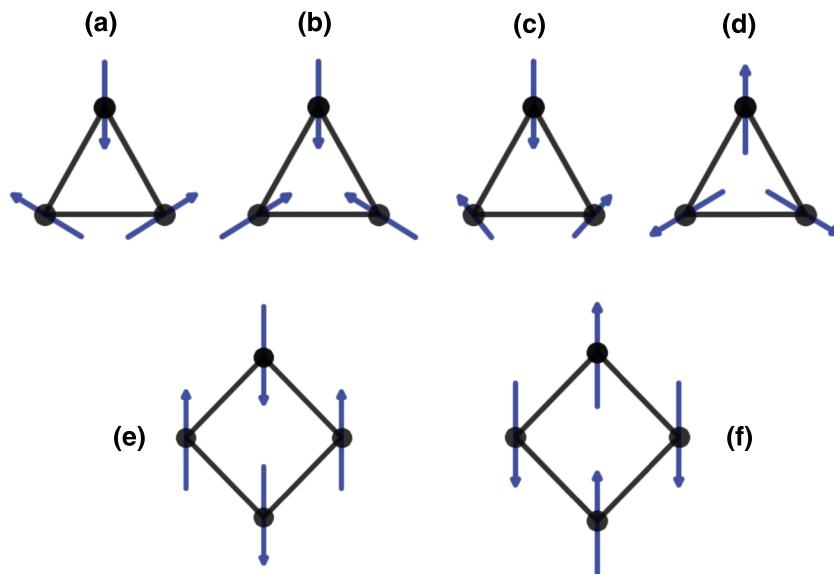


FIG. 4. GHF magnetizations of several degenerate microstates for  $H_3$  (a)–(d) and  $H_4$  ((e) and (f)). The uppermost magnetization vector of each microstate is arbitrarily aligned to the “laboratory  $z$ -axis.” For  $H_3$ , several microstates were found that break the collinearity characteristic to  $\hat{S}_z$  symmetry invariance. For  $H_3$ , (a),(b), and (d) lie in the plane of the page, however, (c) has magnetization vectors that go out of plane. For  $H_4$ , GHF and UHF give the same solution and the microstates are invariant to  $\hat{S}_z$  symmetry. For this reason, only two collinear microstates can be found.

Figure 5. Given this guess, GHF will converge to the collinear UHF solution. However, this GHF solution is a higher order saddle point, as the subsequent GHF stability test shows four negative roots, and using the update scheme, we generate a rotated spin guess, a mere  $0.5 \text{ kcal mol}^{-1}$  ( $\langle S^2 \rangle = 57.9$ ) lower in energy. This rotation breaks the collinearity of the UHF solution, and is enough to perturb the solution to converge to the noncollinear GHF state, which is  $7 \text{ kcal mol}^{-1}$  lower in energy than the UHF reference. Further tests show that this solution is a GHF local minima. This same procedure will be important when studying induced non-collinear magnetism by surface-deposited transition metal nanostructures. Lounis<sup>34</sup> has indicated that Cr and Mn are excellent candidates for non-collinear magnetic structures, but Fe and Ni will not. Clearly, there are many factors to consider in further theoretical study

of such nanostructures, but GHF may play an important role in future work as we see the need to break  $\hat{S}_z$  symmetry for energetically superior results.

#### IV. CONCLUSIONS

Here, we have implemented a complex generalized Hartree-Fock stability test and orbital update scheme in order to seek out the lowest local energetic minima possible within the Hartree-Fock model. We have applied this methodology to simple geometrically frustrated systems, where spin magnetic moments cannot favorably align within the collinear framework. The noncollinearity of the GHF solutions relaxes the symmetry constraints of the exact Hamiltonian, allowing for spin magnetizations to align most favorably in three dimensions. However, despite the energetic advantages of relaxing symmetry constraints, we do so at the loss of good spin quantum numbers. The loss of good spin quantum numbers can be restored at the multideterminantal level, however, it is important to keep in mind that in the true relativistic Dirac formalism, spin is no longer a good quantum number anyway. GHF is inherently a two-component spinor method, and in fact may be thought of as a non-relativistic approximation to two-component Dirac-Fock methods. GHF is critical to the proper description of noncollinear magnetism in transition metal structures, illustrated here for the case of  $Cr_3$ . GHF will be useful for future work involving complex and exotic magnetic systems.

#### ACKNOWLEDGMENTS

The development and application of the two-component electronic structure method are supported by the Department of Energy under the Contract No. DE-SC0006863 to X.L. The computing resources and educational activities are funded by the US National Science Foundation (CHE-1265945, Graduate Research Fellowship DGE-1256082 to J.J.G.). Additional software support from Gaussian, Inc. is gratefully acknowledged.

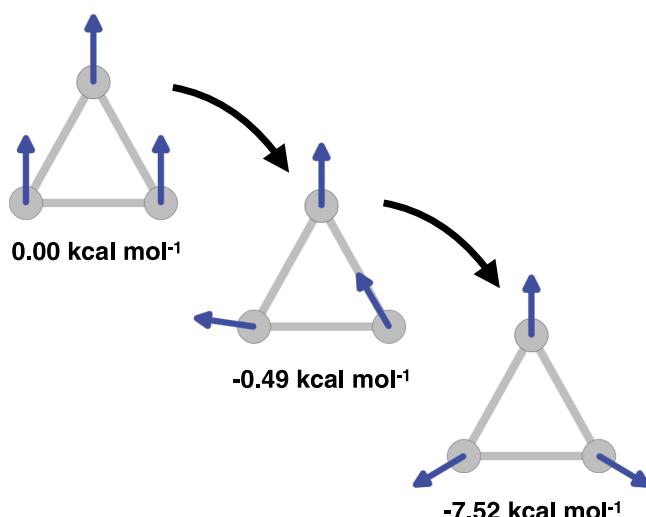


FIG. 5. Connection between higher order GHF solutions in the neutral chromium trimer (LANL2DZ,  $D_{3h}$ ,  $2.89 \text{ \AA}$ ). There exists a high spin GHF solution (left), which also lies in the UHF manifold, that preserves collinearity. However, GHF stability tests indicate a lower solution exists, and the update scheme breaks the collinearity, slightly lowering the energy in the process (center). Subsequent iterations in the SCF bring this noncollinear rotated guess to the true GHF noncollinear minima (right).

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