# Holomorphic Hartree−Fock Theory and Configuration Interaction

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ABSTRACT: We investigate the Hartree−Fock solutions to H_2 in a minimal basis. We note the properties of the solutions and their disappearance with geometry and propose a new method, called Holomorphic Hartree−Fock theory, where we modify the self-consistent field (SCF) equations to avoid disappearance of the solutions. We use these solutions as a basis for a nonorthogonal configuration interaction to produce a smooth binding curve over a complete range of geometries.
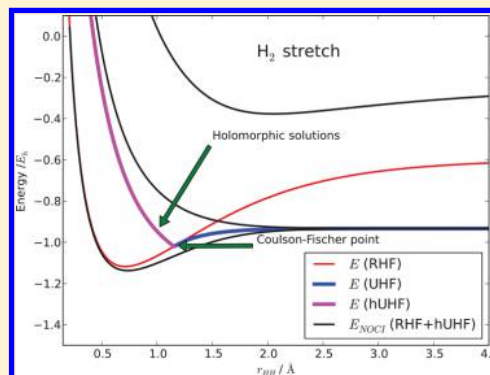
1. INTRODUCTION

Self-consistent field (SCF) electronic structure methods, which include Hartree−Fock (HF) and density functional approximations (DFAs) are presently the bedrock of quantum chemistry, whether they are used in their own right or as a foundation for more-accurate correlation treatments. In essence, applying an SCF method equates to minimizing an energy functional with respect to varying a set of orbitals within a given basis. This is often recast as an iterative diagonalization procedure, but it may also be regarded as a (matrix) polynomial whose roots are to be found, and this procedure is equivalent to locating the stationary points of the energy, with respect to nontrivial changes of the orbitals. It has long been known that, because of this nonlinear form, the SCF equations admit to many solutions, and recently we and other researchers have been interested in both finding the solutions[1] as well as in their physical meaning[2−6] and other uses.[7,8]

It is somewhat surprising to us that, except for some relatively unknown theoretical studies,[9−11] the nature, number, and existence properties of the SCF solutions are basically unknown, especially given that they are so fundamental in quantum chemistry. A typical SCF calculation might involve constructing a density guess and then iterating the SCF until convergence. The more fastidious computational chemist will perform a stability analysis[12,13] to ensure that such solutions are indeed local minima, continuing downward in energy until a local minimum is found. The range of SCF convergence methods commonly used[14−17] makes no guarantee that a global minimum is found, and aside from the recent work of Veeraraghavan and Mazziotti,[18] which can provide upper and lower bounds to solutions, the main effective approach to testing whether a given solution is the lowest energy is by some form of random searching,[1,19−21] which is very seldom done (or at least documented in the literature). In response to Thom and Head-Gordon's SCF metadynamics work on locating SCF solutions,[1] Li and Paldus produced a careful series of

papers[22−24] that investigated the broken symmetry solutions of homonuclear diatomics and ABA triatomics using Thouless stability anaylsis,[12] and, more recently, there have been many investigations of broken symmetry solutions[25−27] and restoration of symmetry.[28] Despite this work, there is little acknowledgment of the existence of many SCF solutions in the wider computational community.

Thus, the most common approach to this multitude of solutions appears to be to mostly ignore them. In transition-metal compounds, for example, we have certainly found solutions[31] which are lower in energy than the local minima found from common guesses, and we suspect this to be a widespread problem. Figure 1 shows, for example, several
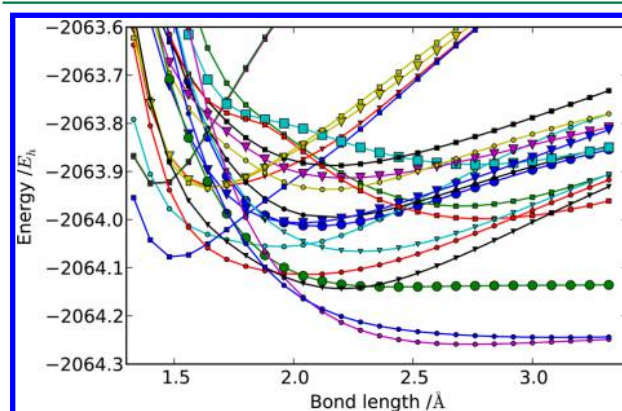

Figure 1. Singlet restricted Hartree-Fock (RHF) solutions for Cr_2 in the STO-3G basis.[29] Solutions were located via metadynamics and curve-following. Curves with small markers are multiply degenerate and large markers are singly degenerate. There is no guarantee that this list of states is exhaustive.

restricted Hartree-Fock (RHF) states of the chromium dimer in a STO-3G basis that cross at different geometries, with four different states having the lowest energy at some point along the binding curve.

While the existence of many SCF solutions might just appear to be an irksome problem in SCF theory, many authors[2−5] have sought to interpret the higher-energy solutions as corresponding to excited states of the system, and, when present, the SCF solutions do indeed appear to correspond to physical states of the system. Motivated by this, one of us has shown that, in some systems, the SCF solutions can be interpreted as quasidiabatic states, and used them as a basis for (non-orthogonal) configuration interaction (CI) calculations,[7,25,32] where they reproduce avoided crossing and conical intersections.

However, such calculations are more generally thwarted by coalescence and disappearance of solutions (for example, at the Coulson−Fischer point[33]), causing discontinuities in binding curves. Figure 2 shows the nonorthogonal configuration
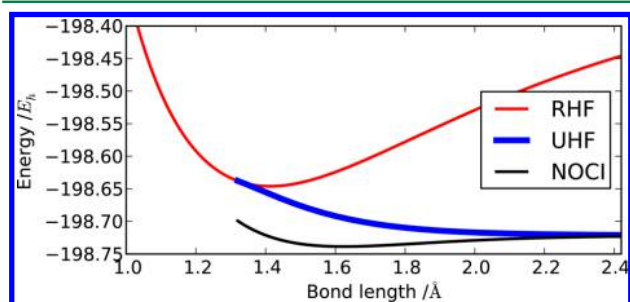

Figure 2. RHF and UHF (doubly degenerate) solutions of F_2 in a cc-pVDZ basis.[30] The black line gives the lowest solution when these are used together as a basis for NOCI. Where only the RHF solution exists, the NOCI solution will correspond to that.

interaction (NOCI) of the restricted Hartree-Fock (RHF) and unrestricted Hartree-Fock (UHF) solutions for the F_2 molecule, which are extremely plausible until the Coulson−Fischer point. Therefore, understanding the disappearance of these solutions is crucial if they are to be used as such or interpreted as anything other than artifacts. [We note, in passing, that, although the recent Projected Hartree−Fock (PHF) work of Scuseria et al.,[26−28] which develops the Complex Molecular Orbital method of Hendeković,[34] follows a similar style of methodology to nonorthogonal configuration interaction (NOCI), the two methods are quite distinct. PHF applies Variation After Projection, where parametrized non-orthogonal wave functions of broken symmetry are constructed. The symmetry is then restored by projection and the energy evaluated. This energy is a function of initial parametrized wave functions and is then variationally optimized by changing these parameters. In NOCI, the determinants are first variationally optimized (by being stationary points of the HF energy) and used in a NOCI, which restores the symmetry (effectively a projection); thus, this is a Projection After Variation method.]

In this paper, we go back to basics and thoroughly investigate the solutions to one of the simplest chemical systems, H_2, in a minimal basis. We note the properties of the solutions and their disappearance with geometry and propose a new method, called Holomorphic Hartree−Fock theory, where we modify the SCF equations to avoid disappearance of the solutions. With a fixed number of solutions across the entire binding

curve, we conclude by showing that these new solutions can be used as a basis for a NOCI, producing smooth binding curves over a complete range of geometries.

2. COMPUTATIONAL DETAILS

SCF calculations were performed in a modified version of Q-Chem 4.0[35] with additional processing using SymPy[36] and SciPy[37] and figures plotted with matplotlib.[38]

3. SCF EQUATIONS

Beginning with the single-particle basis set in three-dimensional (3-D) space, denoted $\chi_\mu(\mathbf{r})$ and generally constructed from atom-centered functions, we may construct an orthonormal basis, $\tilde{\chi}_\mu$, which spans the same space, and express other functions, such as molecular orbitals, as an expansion in this basis,

$$\phi_i = \sum_\mu \tilde{\chi}_\mu C^\mu_{\cdot i} \tag{1}$$

where we are using the tensor notation of Head-Gordon et al.,[39] and will use the Einstein summation convention for repeated indices when no explicit summation is specified. Here, the coefficients $C^\mu_{\cdot i}$ may be complex, and, as the basis χ_μ increases toward the complete, any complex-valued function in the Hilbert space may be expanded in this form.

In this paper, we will primarily be concerned with the Hartree−Fock Self-Consistent Field Approximation, the algorithm and equations for which can be formulated as follows:

(1) Begin with a guess for coefficients $C^\mu_{\cdot i}$.

(2) Form the one-particle density matrix $P^{\mu\nu} = \sum_i^N C^\mu_{\cdot i} C^{*\mu}_i$.

(3) The energy is formed as a functional of density $E(P^{\mu\nu})$:

$$E = h_{\mu\nu} P^{\nu\mu} + \frac{1}{2} P^{\mu\sigma} \Pi_{\mu\nu\sigma\tau} P^{\nu\tau} \tag{2}$$

where the one-electron integrals are defined as $h_{\mu\nu} = \langle \tilde{\chi}_\mu | \hat{h} | \tilde{\chi}_\nu \rangle$ for $\hat{h}$ containing kinetic energy and external potential operators, and the two-electron antisymmetrized Coulomb integrals are $\Pi_{\mu\nu\sigma\tau} = \langle \mu\nu | \sigma\tau \rangle - \langle \mu\nu | \tau\sigma \rangle$ for

$$\langle \mu\nu | \sigma\tau \rangle = \int\int \frac{\tilde{\chi}^*_\mu(\mathbf{r}_1)\tilde{\chi}^*_\nu(\mathbf{r}_2)\tilde{\chi}_\sigma(\mathbf{r}_1)\tilde{\chi}_\tau(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \, \mathrm{d}^3\mathbf{r}_1 \, \mathrm{d}^3\mathbf{r}_2 \tag{3}$$

(4) We solve for $\mathrm{d}E/\mathrm{d}P^{\mu\nu} = 0$ (keeping number of electrons fixed), commonly leading to an iterative set of diagonalizations.

Although not normally written as such, the equations can be equally well written as a function of the coefficients $C^\mu_{\cdot i}$ by including orthogonality of the orbitals in a Lagrangian:

$$\Lambda = E[C^\mu_{\cdot i}] - \sum_{ij} \lambda_{ij}(C^{*\mu}_i C^\mu_{\cdot j} - \delta_{ij}) \tag{4}$$

and solving $\mathrm{d}\Lambda/\mathrm{d}C^\mu_{\cdot i}$, resulting in a coupled set of polynomials in coefficients C. It is this formulation that we would like to consider.

4. SELF-CONSISTENT FIELD (SCF) EQUATIONS FOR H_2

For the very simple case of H_2 in a minimal basis (here, we choose STO-3G[40]) with a single atomic orbital sited on each atom, it is well-known that as the bond length increases past the Coulson−Fischer point, the restricted Hartree−Fock solution (where both α and β spin molecular orbitals have the same spatial form) becomes unstable, with respect to a symmetry-

broken unrestricted Hartree—Fock solution where the α and β molecular orbitals move to become localized on separate atoms. A convenient representation for these solutions is to consider the two orbitals as consisting of rotations of the symmetry orbitals, σ_g and σ_u:

$$\phi_\alpha = \sigma_g \cos \theta + \sigma_u \sin \theta \tag{5}$$

$$\phi_\beta = \sigma_g \cos \theta - \sigma_u \sin \theta \tag{6}$$

This is shown in Figure 3. Here, there is a single electronic degree of freedom, parametrized by θ, and for a given
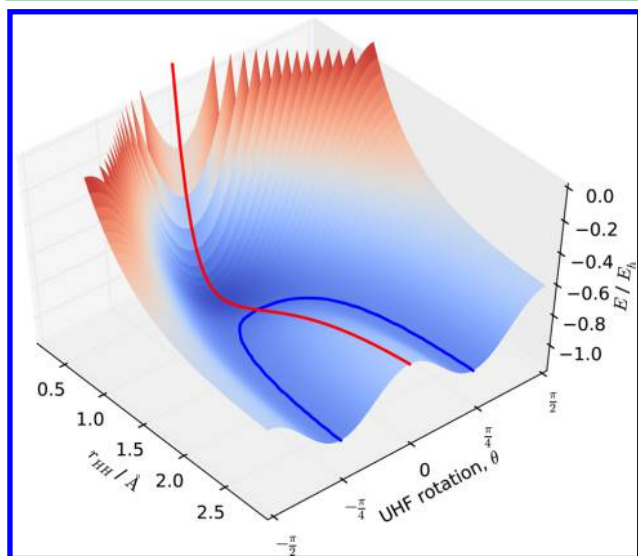

Figure 3. Energy surface for H_2. UHF rotation indicates the angle θ by which the α molecular orbital (αMO) has mixed together the σ_g and σ_u orbitals as specified in the text. The red curve shows the RHF solution as a local minimum against rotation for $r_{HH} < 1.2$ Å, becoming a maximum after this; the blue curves are the two degenerate UHF solutions.

geometry, we may plot energy against this parameter and find the solutions to the SCF equations, being the stationary points of these functions. Two such curves are given in Figure 4. Given the form of the curves, it is tempting to see these as quartic polynomials in θ with one and real three roots. Recalling the Fundamental Theorem of Algebra, which states that every nonzero, single-variable, degree-n polynomial with complex coefficients has, counted with multiplicity, exactly n roots, we speculated that the missing roots might correspond to orbitals with complex coefficients. To investigate this further, it is convenient to transform to a different parametrization and we choose to write the orbitals in terms of a (complex) parameter z,

$$\phi_\alpha = \frac{1}{\sqrt{1 + |z|^2}} \sigma_g + \frac{z}{\sqrt{1 + |z|^2}} \sigma_u \tag{7}$$

$$\phi_\beta = \frac{1}{\sqrt{1 + |z|^2}} \sigma_g - \frac{z}{\sqrt{1 + |z|^2}} \sigma_u \tag{8}$$

where z can be equated with $\tan \theta$. For this system, taking advantage of the symmetry of the integrals, the energy becomes a function of z,
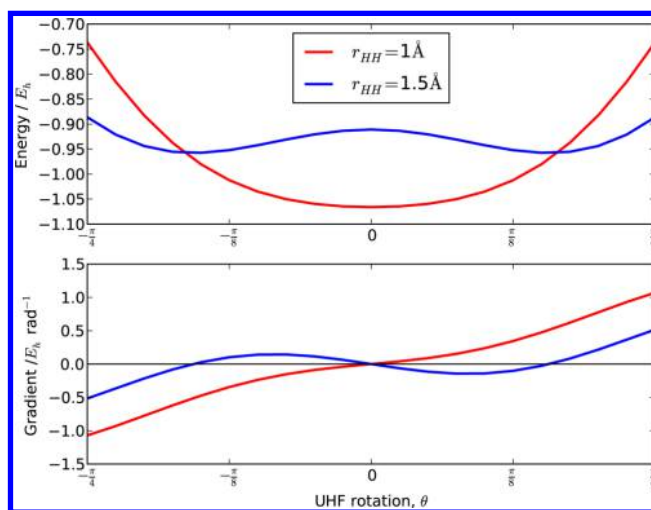

Figure 4. Two slices through the energy surface for H_2, before (red, $r_{HH} = 1$ Å) and after (blue, $r_{HH} = 1.5$ Å) the Coulson—Fischer point, showing the energy (top) and gradient with respect to orbital rotation (bottom), showing one (red) and three (blue) stationary points.

$$E(z) = \frac{2}{1 + z\bar{z}}(h_{gg} + z\bar{z}h_{uu}) + \frac{1}{(1 + z\bar{z})^2}$$
$$\times (\langle gg|gg \rangle - (z^2 + \bar{z}^2)\langle gg|uu \rangle + (z\bar{z})^2 \langle uu|uu \rangle$$
$$+ 2z\bar{z}\langle gu|gu \rangle - 2z\bar{z}\langle gu|ug \rangle)$$

where $\bar{z}$ is the complex conjugate of z. Since $E(z)$ is purely real, we might hope that we can locate solutions $dE(z)/dz = 0$, where z is complex; since $\bar{z}$ is simply a function of z, it is not independent and does not need to be explicitly considered. Indeed, since $E(z)$ is a strictly real function, using $z = x + iy$, it can be viewed as a surface $E(x,y)$ which has stationary points that can be located by standard methods.

A plot of the energy surfaces for $r_{HH} = 1$ Å and $r_{HH} = 1.5$ Å are given in Figure 5. While this view is appealing, as can be seen in the figure, it unfortunately does not lead to finding any additional complex solutions. To understand why, we must consider E to be a complex function.

5. HOLOMORPHIC FUNCTIONS

Despite the energy $E(z)$ being a real function of z by construction, in general, functions of complex variables are usually complex-valued, and such functions and their derivatives are the subject of the theory of complex analysis. While a full exposition of the field is beyond the scope of this paper, there are many useful results that it can bring to bear. Primarily, it should be noted that not all functions of complex variables have well-defined complex derivatives, and only a subset of functions that obey the Cauchy—Riemann conditions are differentiable.

The most relevant form of these conditions in this case is the following: a function $f(z)$ of complex variable z is complex-differentiable if it has no dependence on $\bar{z}$ Such a complex-differentiable function is known as *holomorphic*. Immediately, we can see that the energy function $E(z)$ does not satisfy these conditions. Unfortunately, the Fundamental Theorem of Algebra, which guarantees that complex solutions will exist, is only valid for holomorphic polynomials (which do not contain any explicit $\bar{z}$ dependence), and this is why we have not been able to locate further complex solutions for this energy function.
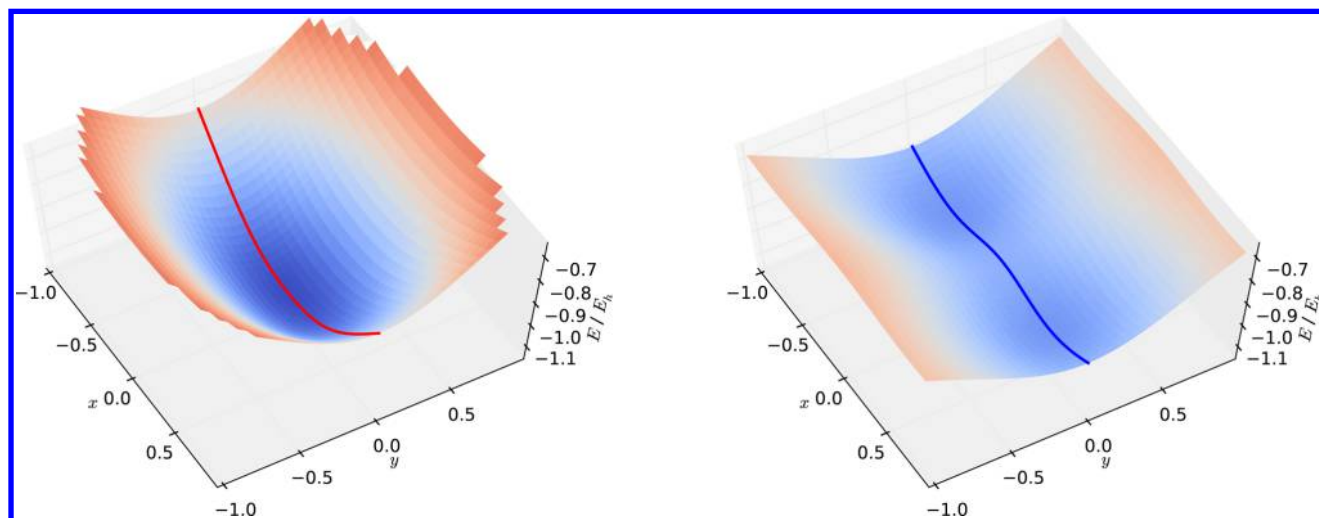
Figure 5. Energy surface for complex $z = x + iy$ for (left) $r_{HH} = 1$ Å and $r_{HH} = 1.5$ Å. There are no additional minima at complex z. The colored curves correspond to those described in Figure 4.
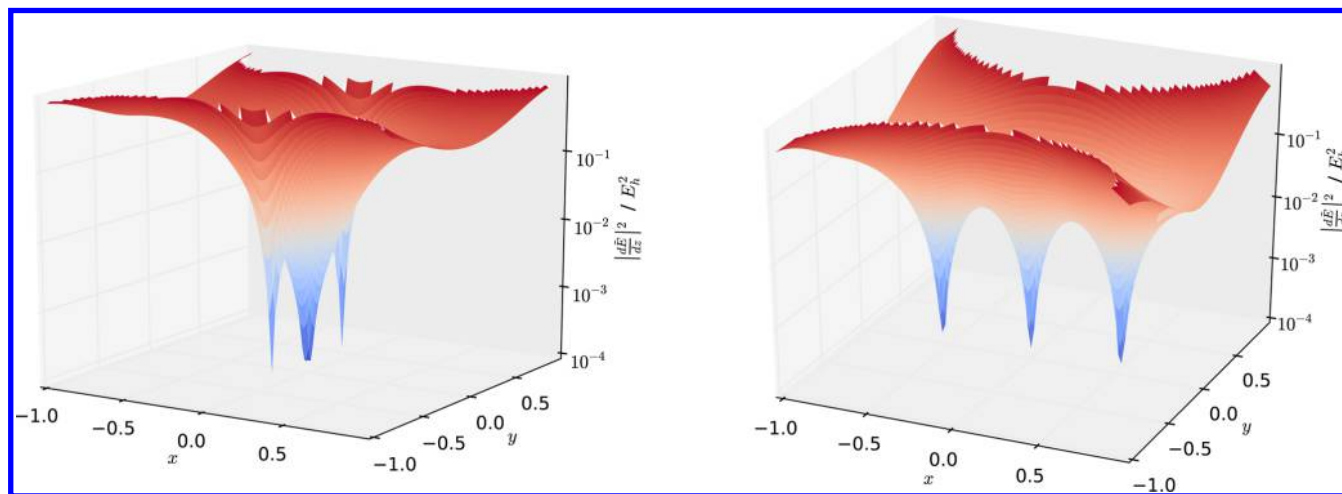

Figure 6. Square magnitude of the gradient of the holomorphized energy $\tilde{E}(z)$ plotted in the complex plane $z = x + iy$. The left picture shows $r_{HH} = 1$ Å with a root at $z = 0$ and two additional roots at $z = \pm0.361110i$; the right shows $r_{HH} = 1.5$ Å with the conventional solutions, $z = 0, \pm0.536989$.

This problem immediately presents its own solution; however, in that if we wish to rely on the Fundamental Theorem of Algebra, we must convert the energy expression into one that is not dependent on $\bar{z}$. We may do this by creating $\tilde{E}(z)$ from $E(z)$ by replacing all instances of $\bar{z}$ with z and call this process *holomorphizing*. A consequence of this is that $\tilde{E}(z)$ is no longer a real-valued function, although we note that (i) where z is real (i.e., for all stationary points of E), $\tilde{E}$ will take the same value as E, and (ii) because of complex conjugation symmetry, z will still be stationary in the imaginary direction, so no stationary points of the original E have been lost.

Being complex-valued, the $\tilde{E}$ surface is extremely difficult to visualize, so, instead, we plot the square magnitude of the derivative of the surface in Figure 6. On both sides of the Coulson–Fischer point, there are the same number of zeroes of gradient (we denote these as holomorphic UHF (hUHF) solutions), with the additional ones at $r_{HH} = 1$ Å having complex orbitals.

For this system, it is trivial to locate these hUHF solutions across the entire range of r_{HH}; these are plotted in Figure 7. It can be seen that the holomorphic energies $\tilde{E}$ are manifestly not variational and, at small bond lengths, are lower than the RHF

energies. We note that the hUHF $\tilde{E}$ do not diverge to negative infinity, but have a minimum at ~0.2 Å and then increase. With the orbitals corresponding to the hUHF solutions, the real energy E can be calculated, and it is found to vary continuously, and (as is required) is higher than the RHF energy before the Coulson–Fischer point. After the Coulson–Fischer point, the hUHF solutions correspond exactly to the UHF solutions, and therefore provide a set of solutions that exist at all geometries.

We note that this holomorphization procedure can be generalized to more-complicated systems and, with a wave function Φ (with complex conjugate $\bar{\Phi}$), the energy functional is

$$E_{hUHF}(\Phi) = \frac{\langle\bar{\Phi}|\hat{H}|\Phi\rangle}{\langle\bar{\Phi}|\Phi\rangle}$$

the stationary points of which give the hUHF solutions.

6. NONORTHOGONAL CONFIGURATION INTERACTION (NOCI)

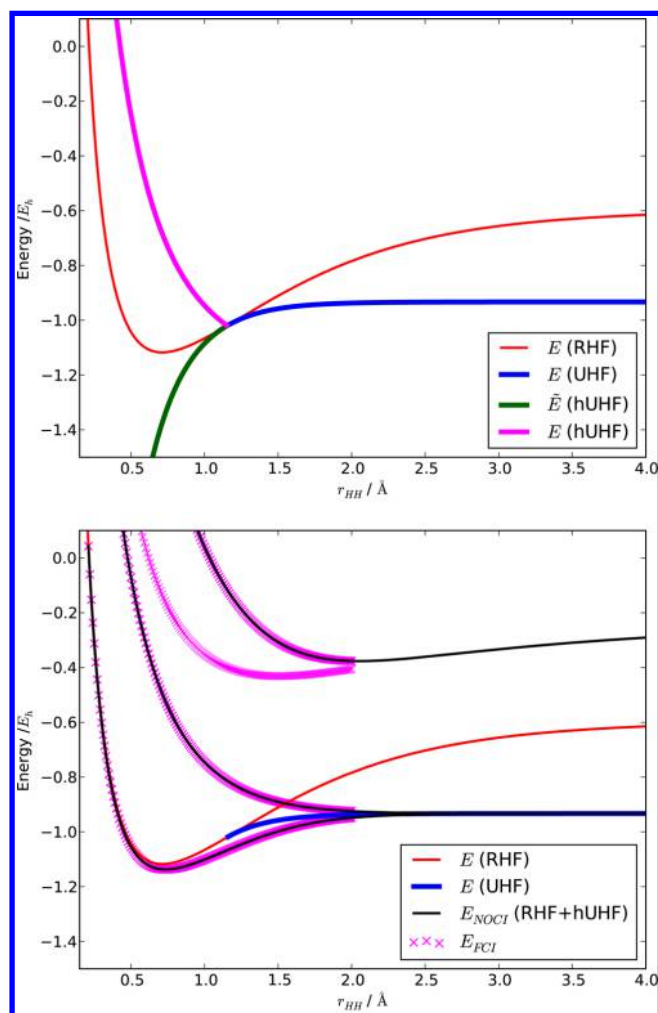The motivation for this study of HF solutions arose from using them in a nonorthogonal configuration interaction (NOCI)[7]

Figure 7. (Left) A comparison of energies for H_2 for RHF, UHF, and holomorphic UHF (hUHF) stationary points. For hUHF, the holomorphic energy $\tilde{E}$ and the real energy E are plotted for the same orbitals. For $r_{HH} > 1.15$ Å, the hUHF are identical to the UHF solutions. (Right) Energies from a nonorthogonal configuration interaction (NOCI) of the RHF and hUHF solutions, which are identical to a subset of the $M_S = 0$ full CI energies in this basis. The symmetries of the FCI states are (from the bottom) $^1\Sigma_g^+$, $^3\Sigma_u^+$, $^1\Sigma_u^+$, $^1\Sigma_g^+$.

and the difficulties caused by such solutions disappearing. By solving the hUHF equations, we have a modified theory which (for this system) has a constant number of solutions as geometry changes, and so these are eminently amenable as a basis for describing molecular dissociation. Using the three hUHF solutions as a basis for CI, we can construct the Hamiltonian and overlap matrices in this basis (being 3 × 3 matrices), and solve the generalized eigenvalue problem to recover energies. We refer the reader to ref 7 for details regarding how to perform this calculation.

The results are plotted in the right-hand side of Figure 7, and compared to the full CI in this basis (with the restriction that $M_S = 0$). We find that the hUHF-NOCI solutions provide identical, and most importantly, smooth curves for three of the FCI states. [We note that, in this small example set, which is composed of the two hUHF and single RHF solutions, the curves happen to span the subspace from the two $^1\Sigma_g^+$ and the $M_S = 0$ $^3\Sigma_u^+$ solution which results in this smoothness. However, this spanning is by no means required of the formalism, and a simple thought experiment performed with the addition of an

extra determinant (for example, constructed from two p-orbitals) which couples to the FCI space would change the FCI energies, but not the hUHF-NOCI energies, and so the smoothness would be maintained in this larger space.] Including any of the higher remaining UHF or RHF states in the NOCI recovers the remaining FCI solution.

7. CONCLUSION

We have demonstrated that the Hartree−Fock self-consistent field (SCF) equations can be modified to be holomorphic, which, in this case, with a single degree of freedom, admit to a constant number of solutions across geometries. Where RHF and UHF solutions exist, the holomorphic solutions are identical; however, at geometries when conventional SCF solutions disappear, complex holomorphic solutions appear. These solutions are stationary values of the nonvariational holomorphic energy, but have real energy expectation values that are above the lowest RHF solution. Crucially, these solutions can be used as a basis for nonorthogonal configuration interaction (NOCI) and have been shown to provide smooth energy curves.

For larger systems, where there are more parameters coupled together, we know of no guarantee of a constant number of solutions; nonetheless, we believe that they may share some of the beneficial properties of the single parameter case, and generalizations of this holomorphized approach using more conventional solution techniques are under investigation.

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Notes

The authors declare no competing financial interest.

■ REFERENCES

(1) Thom, A. J. W.; Head-Gordon, M. *Phys. Rev. Lett.* **2008**, *101*, 193001-1−193001-4.

(2) Besley, N. A.; Gilbert, A. T. B.; Gill, P. M. W. *J. Chem. Phys.* **2009**, *130*, 124308-1−124308-7.

(3) Gilbert, A. T. B.; Besley, N. A.; Gill, P. M. W. *J. Phys. Chem. A* **2008**, *112*, 13164−13171.

(4) Ershova, O. V.; Besley, N. A. *Chem. Phys. Lett.* **2011**, *513*, 179−183.

(5) Hanson-Heine, M. W. D.; George, M. W.; Besley, N. A. *J. Chem. Phys.* **2013**, *138*, 064101-1−064101-8.

(6) Barca, G. M. J.; Gilbert, A. T. B.; Gill, P. M. W. *J. Chem. Phys.* **2014**, *141*, 111104-1−111104-4.

(7) Thom, A. J. W.; Head-Gordon, M. *J. Chem. Phys.* **2009**, *131*, 124113-1−124113-5.

(8) Krausbeck, F.; Mendive-Tapia, D.; Thom, A. J. W.; Bearpark, M. J. *Comp. Theor. Chem.* **2014**, *1040−1041*, 14−19.

(9) Fukutome, H. *Prog. Theor. Phys.* **1971**, *45*, 1382−1406.

(10) Fukutome, H. *Int. J. Quantum Chem.* **1981**, *20*, 955−1065.

(11) Mestechkin, M. *J. Mol. Struct. (THEOCHEM)* **1988**, *181*, 231−236.

(12) Thouless, D. J. *Nucl. Phys.* **1960**, *21*, 225−232.

(13) Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1977**, *66*, 3045−3050.

(14) Pulay, P. *Chem. Phys. Lett.* **1980**, *73*, 392−398.

(15) Kudin, K. N.; Scuseria, G. E.; Cancès, E. *J. Chem. Phys.* **2002**, *116*, 8255.

(16) Roothaan, C. C. J. *Rev. Mod. Phys.* **1951**, *23*, 69−89.

(17) Høst, S.; Jansík, B.; Olsen, J.; Jørgensen, P.; Reine, S.; Helgaker, T. *Phys. Chem. Chem. Phys.* **2008**, *10*, 5344−5348.

(18) Veeraraghavan, S.; Mazziotti, D. A. *Phys. Rev. A* **2014**, *89*, 010502(R)−1−5.

(19) de Andrade, M. D.; Mundim, K. C.; Malbouisson, L. A. C. *Int. J. Quantum Chem.* **2005**, *103*, 493−499.

(20) de Andrarade, M. D.; Nascimento, M.; Mundim, K.; Malbouisson, L. *Int. J. Quantum Chem.* **2006**, *106*, 2700−2705.

(21) Malbouisson, L. A. C.; de Cerqueira Sobrinho, A. M.; Nascimento, M. A. C.; de Andrade, M. D. *Appl. Math.* **2012**, *3*, 1526−1531.

(22) Li, X.; Paldus, J. *J. Chem. Phys.* **2009**, *130*, 084110−1−9.

(23) Li, X.; Paldus, J. *Int. J. Quantum Chem.* **2009**, *109*, 1756−1765.

(24) Li, X.; Paldus, J. *Phys. Chem. Chem. Phys.* **2009**, *11*, 5281−5289.

(25) Sundstrom, E. J.; Head-Gordon, M. *J. Chem. Phys.* **2014**, *140*, 114103-1−114103-11.

(26) Cui, Y.; Bulik, I. W.; Jiménez-Hoyos, C. A.; Henderson, T. M.; Scuseria, G. E. *J. Chem. Phys.* **2012**, *139*, 154107-1−154107-10.

(27) Jiménez-Hoyos, C. A.; Henderson, T. M.; Scuseria, G. E. *J. Comput. Theor. Chem.* **2011**, *7*, 2667−2674.

(28) Jiménez-Hoyos, C. A.; Henderson, T. M.; Tsuchimoci, T.; Scuseria, G. E. *J. Chem. Phys.* **2012**, *136*, 164109-1−164109-13.

(29) Pietro, W. J.; Hehre, W. J. *J. Comput. Chem.* **1983**, *4*, 241−251.

(30) Dunning, T. H., Jr. *J. Chem. Phys.* **1989**, *90*, 1007−1023.

(31) Thom, A. J. W.; Sundstrom, E. J.; Head-Gordon, M. *Phys. Chem. Chem. Phys.* **2009**, *11*, 11297−11304.

(32) Malmqvist, P. A. *Int. J. Quantum Chem.* **1986**, *30*, 479−494.

(33) Coulson, C. A.; Fischer, I. *Philos. Mag.* **1949**, *40*, 386.

(34) Hendeković, J. *Int. J. Quantum Chem.* **1974**, *8*, 799−815.

(35) Shao, Y.; et al. *Mol. Phys.* **2014**, DOI: 10.1080/00268976.2014.952696.

(36) SymPy Development Team. *SymPy: Python Library for Symbolic Mathematics*; 2014.

(37) Jones, E.; Oliphant, T.; Peterson, P. *SciPy: Open Source Scientific Tools for Python*; 2001.

(38) Hunter, J. D. *Comput. Sci. Eng.* **2007**, *9*, 90−95.

(39) Head-Gordon, M.; Maslen, P. E.; White, C. A. *J. Chem. Phys.* **1998**, *108*, 616−625.

(40) Hehre, W. J.; Stewart, R. F.; Pople, J. A. *J. Chem. Phys.* **1969**, *51*, 2657−2664.

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