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Finding symmetry breaking Hartree-Fock solutions: The case of triplet instability

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Determining the lowest unrestricted Hartree-Fock (UHF) solution is often difficult in even-electron systems. We have developed a deterministic method for locating approximately the UHF minimum using the restricted Hartree-Fock triplet instability matrix. The current method is truncated to fourth order. The minimum energy solution for this model can be determined by solving a small linear system of equations. This solution gives a suitable starting point to determine the exact UHF solution. This should be useful for the black-box determination of active spaces spanned by the fractionally occupied charge natural orbitals of the ground-state UHF wavefunction. The results can be generalized to higher (6th and 8th) degree expansions (odd expansion orders vanish by symmetry), and to other types of instability, including complex instability. The results are illustrated by calculations on ozone, benzene, nitrobenzene, butadiene, hexatriene, octatetraene, dichromium, and nickel porphine. Further examples are given in the supplementary material. *Published by AIP Publishing.* [http://dx.doi.org/10.1063/1.4964903]

I. INTRODUCTION

In spite of the tremendous success of electronic structure theory, systems with strong electron correlation still present a serious problem to accurate computational models. Density functional theory (DFT) often yields reasonable solutions in less severe cases, but its restriction to single configurations precludes the direct calculation of a number of important systems such as open-shell singlets, and in general low-spin open shell molecules. Strongly correlated systems are of crucial importance in processes where chemical bonds are formed and broken, and in redox reactions. Transition metal complexes, widely used as redox catalysts, are usually strongly correlated. A number of important systems derive their utility from the low highest occupied molecular orbital (HOMO)-lowest unoccupied molecular orbital (LUMO) gap which leads to strong correlation.

In strongly correlated systems, the Hartree-Fock (H-F) solution which assigns electrons to the lowest energy molecular orbitals is a poor zeroth-order approximation for the ground state. Strong or nondynamical (static) correlation arises from a modest number of participating orbitals with significant weight, unlike weak or dynamical correlation which is the collective result of a very large number of configurations with small individual weights. Static correlation generally influences potential surfaces qualitatively, unlike dynamical correlation which is important for energy differences but seldom causes large change in the local behavior of potential surfaces. This is easy to understand because the effects of a huge number of configurations tend to cancel, except for the total energy to which each contributes in the same (lowering) sense. The proper starting point in strongly correlated systems is a multiconfigurational wavefunction, which explicitly includes electron correlation (generally via configuration interaction, CI) for the active orbitals, i.e., for those participating in strong electron correlation. With optimized orbitals, this is multiconfigurational self-consistent field (MC-SCF), a generalization of the Hartree-Fock method. MC-SCF had a rocky start and is still not routinely used, for several valid reasons. Early work was plagued with severe convergence problems, due to the strong coupling between the orbital and CI optimization parameters. Convergence was much improved by the complete active space (CAS) concept,[1] based on the full optimized reaction space (FORS)[2] idea of Ruedenberg, and developed in the MC-SCF field as the complete active space self-consistent field (CASSCF) method by Roos and co-workers.[1] Programs like MOLPRO[3] and MOLCAS[4] have largely solved the CASSCF convergence problem.

Unfortunately, the performance of CASSCF leaves much to be desired, both in accuracy and in computational efficiency. As discussed, e.g., in a recent review,[5] CASSCF with the minimum necessary active space is rather imbalanced and exaggerates nondynamical correlation. This error is difficult to correct by adding dynamical correlation later to a CAS wavefunction because CAS readjusts in the presence of dynamical correlation. Extending the active space by including orbitals which are not strongly correlated improves the accuracy, but makes the wavefunction arbitrary and unsuitable for model chemistry. Computationally, CAS scales factorially with the size of the active space, and becomes unmanageable beyond about 18 active orbitals, except for systems with high symmetry (and, consequently, little chemical interest). Another problem plaguing CAS (and all methods which treat a group of orbitals differently from the rest) is that potential surfaces may become discontinuous. As the geometry of the molecule changes, some orbitals which participate in

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strong correlation gradually become inactive, and vice versa.

The greatest problem of CAS is, however, that it is very far from the "black box" ideal.[6] Selecting the proper active space requires a thorough understanding of electronic structure, restricting CAS-type calculations to specialists. A number of attempts have been made to make active space selection more automatic. Such criteria should have a sharp cutoff distinguishing active and non-active orbitals. In our opinion, the method which comes closest to this ideal for ground states is the unrestricted natural orbital (UNO) criterion.[7] For simplicity, we consider here a singlet system. The basis of the UNO criterion is the observation that triplet instability, i.e., the existence of a spin-unrestricted Hartree-Fock (UHF) wavefunction which is lower in energy than the closed-shell restricted Hartree-Fock (RHF) solution, signals the onset of static correlation. It has been shown for a number of typical systems that the fractionally occupied charge natural orbitals (NOs) of the UHF wavefunction closely span the strongly correlated orbital subspace of the molecule. These are the orbitals which should be included in the CAS active space. The relationship between fractional occupancy of NOs and strong correlation was recognized early by Yamaguchi[8,9] before the CAS concept. However, his method of performing a CI in UHF NOs *in the whole orbital space* offers no significant advantage by itself, as the wavefunction and the energy are invariant against transformation to natural orbitals. The UNO-CAS criterion, as formulated by Hamilton and Pulay,[7] applies the active space concept, and offers a black-box definition of the CAS active space as the UHF NOs which have occupancies between 0.01 and 1.99 (or 0.02 and 1.98). These orbitals can be used as starting orbitals for CASSCF, or used directly without the time-consuming orbital optimization step, leading to the UNO-CAS method.[10] UNO-CAS is much more efficient than CASSCF, and generally provides potential surfaces which are slightly above (about 1 mE_h per active orbital) but largely parallel to CASSCF surfaces. We have recently compared the UNO criterion and UNO-CAS and UNO-CAS based CASSCF wavefunctions and energies with large-scale density matrix renormalization group (DMRG) calculations for a number of prototypical strongly correlated systems.[11] These have shown that the UNO criterion works very well. However, it still has the problem of discontinuities. We will return to this problem in a future paper dealing with the half-projected Hartree-Fock natural orbital (HPNO) criterion, continuing work began long ago.[12]

The study of Hartree-Fock instabilities was pursued intensively in the 1960s and 70s by Thouless,[13] Cizek and Paldus,[14] Yamaguchi,[9] Koutecky,[15] Ostlund,[16] Seeger and Pople,[17] and Fukutome[18] However, the success of density functional theory (DFT) in chemistry made it less relevant in the 1990s. As the limitations of DFT became more clearly recognized, and computational power increased, the subject has been taken up anew.[19–21] The objective in these recent contributions is automating active space selection and including strong correlation inexpensively, the same goals that guided the UNO criterion and the UNO-CAS method.

Other types of symmetry breakings are also associated with electron correlation. This is clear from the fact that Hamiltonians without explicit electron-electron interactions

cannot have symmetry-breaking solutions. Singlet instability is generally relevant only in systems with spatial symmetry where the ground-state wavefunction breaks the spatial symmetry. Complex instability, studied recently by the Head-Gordon group,[21] is closely related to triplet instability. Scuseria, in particular, explored a number of symmetry-breaking solutions, including non-collinear spin functions, and even violations of the particle number symmetry.[22] However, as a recent comparison of the UNO criterion with density matrix renormalization group results with large active spaces[11] shows the most important symmetry breaking, which indicates strong correlation is triplet instability. This is easy to understand based on a simple physical picture. Two electrons in the field of the nuclei and the other electrons always occupy the same orbital if there is no repulsion between them, leading to a configuration $|i\bar{i}\rangle$ where the overbar signals β spin. However, if the electronic repulsion between the two electrons is large enough, a configuration with the electrons occupying two different higher energy orbitals may be energetically more favorable, the penalty in the orbital energy being offset by the decrease in interelectronic repulsion. Textbook examples are the splitting of a doubly occupied bonding orbital to different orbitals for α and β electrons as the bond is stretched, or the splitting of a doubly occupied π orbital in ethylene as the dihedral angle approaches 90°. An older but still relevant review was given by Löwdin;[23] for a recent general discussion, see Mayer.[24]

Although the UNO criterion greatly simplifies the selection of the active space, finding the UHF solution, or solutions, is still not simple. A symmetry-adapted closed-shell real wavefunction is always a solution of the UHF equations for an even number of electrons, and the SCF procedure has a tendency to converge to this saddle point, particularly if the DIIS (Direct Inversion in the Iterative Subspace) convergence acceleration method,[25,26] installed in most SCF programs, is used. Imposing spatial symmetry often prevents spin-symmetry breaking. If more than a pair of orbitals participates in static correlation, there may be multiple solutions, depending on how the phases of the symmetry-breaking rotations are combined. The existence of instabilities is indicated by negative eigenvalues of the orbital rotation Hessian corresponding to the type of the instability, but does not give an approximate solution directly. Instability analysis is included in some *ab initio* program suites but was not widely used, probably because of its computational cost. Seeger and Pople[17] describe a univariate search along the negative eigenvalue of the instability matrix to find UHF solutions. It is restricted to a single negative eigenvalue, and cannot exclude other, deeper minima. In more complicated cases, there may be several negative eigenvalues. Liu and Pulay[27] describe a simplified method in which a selected occupied orbital is mixed with all virtuals. This is efficient but cannot always find an existing negative eigenvalue because of it is restricted to a single occupied orbital (generally the highest occupied molecular orbital, HOMO or an orbital close to the HOMO). The restriction was introduced because of the steep computational scaling of the full instability criterion.

Given the recent explosion of computational power, reservations about the computational cost of instability are not

relevant anymore. Moreover, instability is often only weakly dependent on the atomic basis set, and can be determined using modest bases. We develop here a method of mapping the electronic energy surface as a function of symmetry-breaking orbital rotation. We will concentrate on triplet instability, but the same procedure can be also applied to other types of instabilities, in particular complex orbitals. We transform the instability information to a compact form, and prove a theorem which allows us to approximate the Hartree-Fock energy with a simple analytical formula through fifth order. This is used to develop a deterministic algorithm for locating local minima on the UHF energy surface instead of the haphazard way of letting the SCF algorithm try to find them, or a tedious numerical search.

II. TRIPLET INSTABILITY ENERGY SURFACES

In this section, we develop a simple analytical model, valid through fifth order, for the Hartree-Fock energy in the wider vicinity of a closed-shell wavefunction as a function of the orbital rotation angles, which transform the wavefunction to the UHF form. The orbital part of beta spin-orbitals is denoted by an overbar. The indices of occupied orbitals are $i, j, \ldots$, and the virtual indices are $a, b, \ldots$. The original unperturbed closed-shell orbitals are denoted by a superscript ^{0}. Mixing a virtual orbital to an occupied orbital by an angle x_{ia} to create a diradicaloid UHF wavefunction can be accomplished by the pair of orbital rotations

$$\varphi_i(x_{ia}) = \varphi_i^0 \cos(x_{ia}) + \varphi_a^0 \sin(x_{ia}),$$
$$\overline{\varphi_i}(x_{ia}) = \varphi_i^0 \cos(x_{ia}) - \varphi_a^0 \sin(x_{ia}). \tag{1}$$

The overlap of the spatial parts of the alpha and beta orbitals upon mixing by an angle x is $\cos^2 x - \sin^2 x = \cos(2x)$. The total energy can be written as a power series in the rotational angles x_{ia} as follows:

$$E - E^0 = \sum_{ia} \mathbf{g}_{ia} x_{ia}$$
$$+ \tfrac{1}{2} \sum_{ia} \sum_{jb} \mathbf{H}_{ia,jb}\, x_{ia} x_{jb} + \ldots, \tag{2}$$

where E^0 is the energy of the closed-shell determinant. As the closed-shell wavefunction is optimized, the linear term, i.e., the gradient $\mathbf{g}$ vanishes. If the Hessian $\mathbf{H}$ has negative eigenvalues, the closed-shell solution is triplet unstable. Analogous formulas can be derived for other (say complex) instabilities.

Formulas for the orbital Hessian matrix for various instabilities have been derived by several authors.[13,14,17] The dimension of the Hessian is $N_{occ} \times N_{virt}$, where N_{occ} and N_{virt} are the number of occupied and virtual orbitals, respectively, and both, particularly N_{virt} can thus be large. As only the lowest eigenvalues and eigenvectors of $\mathbf{H}$ are of interest, it is best to extract these by an iterative procedure rather than direct diagonalization. The K-th eigenvector of the Hessian, $\mathbf{x}^K$, can be cast in the matrix form as

$$(\mathbf{X}^K)_{ai} = (\mathbf{x}^K)_{a,i}. \tag{3}$$

In the following, we will suppress the superscript K. To determine the participating orbitals, the $N_{virt} \times N_{occ}$ matrix $\mathbf{X}$ is

brought to a diagonal form using singular value decomposition (or the equivalent diagonalization of the square matrices $\mathbf{X}\mathbf{X}^T$ and $\mathbf{X}^T\mathbf{X}$) by the transformation

SVD of the eigenvector

$$\mathbf{D} = \mathbf{U}^T\mathbf{X}\mathbf{V}, \tag{4}$$

where $\mathbf{U}$ and $\mathbf{V}$ are unitary (orthogonal in the real case) matrices of dimensions N_{virt} and N_{occ}, respectively. The matrices $\mathbf{D}$, U, and $\mathbf{X}$ are determined by the singular value decomposition (SVD) of $\mathbf{X}$.[28] $\mathbf{D}$ has N_{occ} non-zero elements along its diagonal; the rest of it is zero (we assume here that $N_{virt} > N_{occ}$). In the following, we omit the last $(N_{virt} - N_{occ})$ rows of $\mathbf{U}^T$ and $\mathbf{D}$ and consider $\mathbf{D}$ and $\mathbf{V}$ $N_{occ} \times N_{occ}$ square matrices, and $\mathbf{U}$ an $N_{virt} \times N_{occ}$ matrix. Transforming the occupied and virtual canonical orbitals, represented by the row vectors $\boldsymbol{\varphi}$ and $\boldsymbol{\chi}$ as

$$\boldsymbol{\varphi}' = \boldsymbol{\varphi}\mathbf{V} \text{ and } \boldsymbol{\chi}' = \boldsymbol{\chi}\mathbf{U} \tag{5}$$

yields the corresponding orbital pairs $\{\varphi_i', \chi_i', i = N_{occ}\}$. An orbital rotation along eigenvector K of the electronic Hessian $\mathbf{H}$ mixes each occupied orbital φ_i' only with its virtual partner χ_i'. The mixing is as in Eq. (1) but the rotational angles are multiplied by the diagonal elements of $\mathbf{D}$. The diagonal elements of D are positive and ≤ 1 in absolute value. The occupied-virtual orbital pairs corresponding to the significant elements of $\mathbf{D}$ span the active space generated by a particular triplet instability. $\mathbf{D}$ has usually only a few significant elements, as will be shown later in the Examples section. Note that there is no direct connection between the significantly split orbital pairs in the converged UHF solution and the number of negative eigenvalues of the electronic Hessian $\mathbf{H}$. The Hessian for benzene, for instance, has only one negative eigenvalue but this has 3 significant components, leading to 3 orbitals significantly split, and to a 6×6 CAS space (the minimum basis in the π space, see Table II).

An orbital rotation along an eigenvector of the Hessian can be defined by the orthogonal transformation

$$\mathbf{R} = \exp \begin{pmatrix} 0 & s\mathbf{X}^T \\ -s\mathbf{X} & 0 \end{pmatrix}, \tag{6}$$

where $\mathbf{X}$ is the instability eigenvector in matrix form, Eq. (3), and the superscript ^{T} denotes the transpose. The parameter s determines the magnitude of the rotation. The first N_{occ} rows and columns of $\mathbf{R}$ correspond to the occupied orbitals, the last N_{virt} to the virtual orbitals. Only the first N_{occ} columns of $\mathbf{R}$ enter the wavefunction.

The calculation of the exponential in Eq. (6) is greatly simplified by the SVD form of $\mathbf{X}$, $\mathbf{X} = \mathbf{U}\mathbf{D}\mathbf{V}^T$ which gives

$$\mathbf{R} = \begin{pmatrix} \mathbf{V} & 0 \\ 0 & \mathbf{U} \end{pmatrix} \begin{pmatrix} \cos(s\mathbf{D}) & \sin(s\mathbf{D}) \\ -\sin(s\mathbf{D}) & \cos(s\mathbf{D}) \end{pmatrix} \begin{pmatrix} \mathbf{V}^T & 0 \\ 0 & \mathbf{U}^T \end{pmatrix}. \tag{7}$$

This formula is the generalization of the rotation matrix of Mayer.[29]

If the electronic Hessian has only one negative eigenvalue then the UHF solution can be readily determined through 5th order in the rotational parameters. It is clear that the expansion of the energy in Eq. (1) can have only even powers, as interchanging the α and β spins, which is equivalent to reversing the signs of all rotational angles in Eq. (1),

should leave the energy unchanged. Thus the knowledge of the quadratic and quartic coefficients of the UHF (or other symmetry-breaking) energy in terms of the symmetry breaking parameter s gives the lowest energy SCF solution *analytically* through fifth order as the minimum of

$$E = E^0 + (1/2)H_{ss} s^2 + (1/24)H_{ssss} s^4. \tag{8}$$

The minimum condition in the variable s^2 gives

$$s = \pm(-6H_{ss}/H_{ssss})^{1/2}, \tag{9}$$

which is real if H_{ss} is negative, i.e., there is an instability, and H_{ssss} is positive. We will show that an analytical solution through fifth order can be obtained also if there are several instabilities, i.e., negative eigenvalues of the Hessian. This is remarkable because the equations to be solved are nonlinear in several variables. Such equations can generally be solved only numerically.

For simplicity, consider a system with two instabilities. The quartic expansion of the energy in terms of the two rotational parameters, s and t, is

$$\begin{aligned}
E(s,t) = {} & E^0 + (1/2)H_{ss} s^2 + (1/24)H_{ssss} s^4 \\
& + (1/2)H_{ss} t^2 + (1/24)H_{ssss} t^4 + (1/4) \\
& \times H_{sstt}s^2t^2 + (1/6)H_{ssst}s^3t + (1/6)H_{sttt}st^3, \tag{10}
\end{aligned}$$

if only even terms are allowed. In the absence of the last two terms, the minimum of Eq. (10) could be determined analytically in terms of the variables s^2 and t^2 as the solution of a 2×2 linear system of equation.

We will give a simplified proof in Sec. III that the derivatives H_{ssst} and H_{sttt} vanish if the rotational parameters are chosen to be along the eigenvectors of the Hessian **H**. This proof assumes that each of the two instabilities consist of only one occupied-virtual rotation, similar to Eq. (1). In other words, the diagonal matrix D in Eq. (4) has only one non-zero element, and its rank is 1. The general proof is more involved and will be published separately.[30] The proof rests on the fact that the derivatives H_{ssst} and H_{sttt} can be written as (for the first one)

$$H_{ssst} = H_{st} F(s,t), \tag{11}$$

where the function F is non-singular at $s, t = 0$. H_{st} vanishes in the eigenvector basis, making the mixed quartic derivatives H_{ssst} and H_{sttt} vanish as well. If both orbital rotations s and t include only two orbitals, an occupied and a virtual one, the function F is simply the numerical constant -4.

TABLE I. The lowest six eigenvalues of the triplet instability matrix for ozone, nitrobenzene, and dichromium using different basis sets.

Ozone		Nitrobenzene		Cr$_2$	
6-31G*	def2-TZVP	6-31G*	def2-TZVP	m6-31G*	def2-TZVP
−0.204 03	−0.203 83	−0.051 13	−0.049 78	−0.202 23	−0.209 38
−0.009 97	−0.012 30	−0.029 30	−0.026 76	−0.141 96	−0.151 68
0.022 85	0.020 44	0.109 26	0.102 69	−0.141 96	−0.151 68
0.061 56	0.053 40	0.121 24	0.117 67	−0.137 81	−0.149 60
0.165 02	0.158 47	0.125 35	0.118 63	−0.096 41	−0.107 89
0.252 28	0.244 39	0.133 90	0.130 74	−0.096 24	−0.107 62

We have verified these results by calculating the derivatives numerically. The numerical values are, of course, not zero but very small. More importantly, they decrease by orders of magnitude when the numerical thresholds are sharpened, indicating that their origin is rounding error. Sec. III gives formulas for quartic derivatives of the SCF energy with respect to triplet instability parameters for orbital rotations, if both rotations are restricted to mixing a single orbital in the occupied space with a single orbital in the virtual space. It appears that these are the first formulas for these quantities. Although the formulas for the quartic derivatives are simple, calculating them numerically is a viable option.

III. HIGHER DERIVATIVES OF SCF ENERGY INSTABILITY SURFACES AND THE DETERMINATION OF SYMMETRY-BREAKING SOLUTIONS

Let us consider two orbital rotations of the type defined in Eq. (1), with φ_a splitting φ_i into different orbitals for α and β spins (rotational angle s), and φ_b splitting φ_j by an angle t. It is straightforward to derive an energy formula for the resulting UHF-type wavefunction, in which all other orbitals are doubly occupied, as a function of the rotational angles s and t. Differentiation of the resulting energy expression at the closed-shell solution ($s = t = 0$) by a symbolic algebra program[31] gives the following results:

$$\frac{1}{4}\left(\frac{\partial^2 E}{\partial s^2}\right) = F_{aa} - F_{ii} - J_{ia} - K_{ia}, \tag{12}$$

$$\frac{1}{4}\left(\frac{\partial^2 E}{\partial s \partial t}\right) = -(ij|ab) - (ib|ja), \tag{13}$$

TABLE II. Negative instability eigenvalues and the greatest singular values of the corresponding eigenvectors for benzene, naphthalene, and nitrobenzene calculated using the def2-TZVPP basis set.

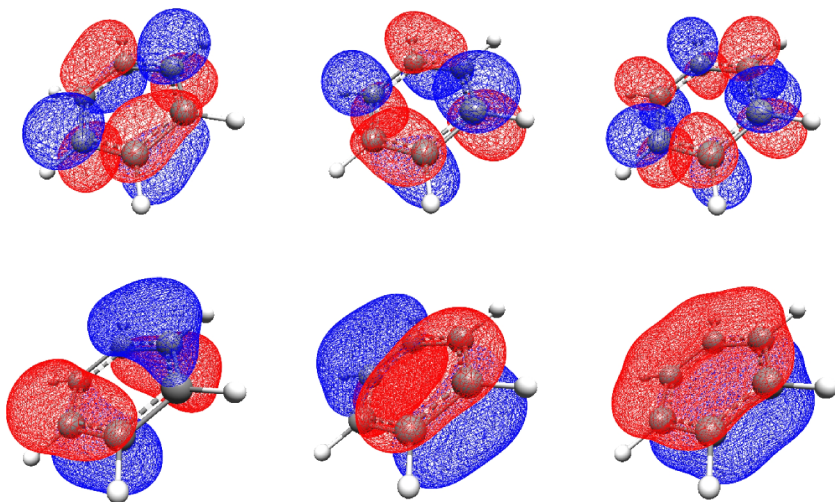| Benzene		Naphthalene		Nitrobenzene	
Eigenvalue	Singular values	Eigenvalue	Singular values	Eigenvalue	Singular values
−0.026 28	0.665 22	−0.046 91	0.684 66	−0.049 78	0.987 36
	0.665 20		0.504 38		0.125 89
	0.302 23		0.371 61		0.056 80
	0.061 89		0.283 23	−0.026 76	0.675 05
	0.061 89		0.191 93		0.651 74
	0.057 11		0.048 04		0.302 84

FIG. 1. Occupied-virtual orbital pairs corresponding to the triplet instability of benzene. The occupied orbitals are in the lower row, the corresponding virtuals are immediately above. The negative eigenvalue is $-0.026\,28$ E$_h$, and its three principal components have diagonal elements of 0.6652, 0.6652, and 0.3022. The other elements of the diagonal matrix **D** in Eq. (4) are small, the largest being 0.0619.

$$\frac{1}{4}\left(\frac{\partial^4 E}{\partial s^4}\right) = 4F_{ii} - 4F_{aa} + 6J_{ii} - 8J_{ia}$$
$$+ 28K_{ia} + 6J_{aa}, \tag{14}$$

$$\frac{1}{16}\left(\frac{\partial^4 E}{\partial s \partial t^3}\right) = (ij|ab) + (ib|ja), \tag{15}$$

$$\frac{1}{8}\left(\frac{\partial^4 E}{\partial s^2 \partial t^2}\right) = 2J_{ab} - 2J_{ja} + 2J_{ij} - 2J_{ib} - K_{ij}$$
$$+ K_{ib} + K_{ja} - K_{ab}, \tag{16}$$

typo here! $\frac{1}{64}\left(\frac{\partial^4 E}{\partial s \partial t^5}\right) = \frac{1}{64}\left(\frac{\partial^4 E}{\partial s^3 \partial t^3}\right) = -(ij|ab) - (ib|ja).$ (17)

The rest of the formulas can be generated by interchanging s and t, and (ia) and (jb). It is assumed here that the molecular orbitals are real. More general results, including complex orbitals, will be given in Ref. 30.

The Mulliken convention is used for the two-electron integrals

$$(pq|st) = \int \int p(\mathbf{r})q(\mathbf{r})\frac{1}{r_{12}}s(\mathbf{r}')t(\mathbf{r}')d^3\mathbf{r}d^3\mathbf{r}'. \tag{18}$$

The Coulomb and exchange integrals are defined as

$$J_{pq} = (pp|qq) \text{ and } K_{pq} = (pq|pq), \tag{19}$$

where F is the Fock matrix, and, in canonical basis, F_{ii} and F_{aa} are the orbital energies. Eq. (15) shows that mixed first-third order derivatives are zero if the mixed second-order derivatives, Eq. (13), vanish, as stated in Sec. II. Mixed sixth-order derivatives containing odd powers of the individual rotations (but being even overall) also vanish, but a sixth-order

expansion makes the determination of the rotational angles iterative. For several instabilities, terms like s^2tu or $stuv$ can in principle contribute to a quartic expansion, but these terms vanish because the total energy contains only pairwise orbital interactions.

The stationary points of a quartic approximation to the UHF energy (actually quintic because fifth-order terms automatically vanish) can be readily obtained. In terms of the squared rotational parameters, the quartic expansion of the UHF energy, Eq. (10), can be written as

$$E(X_1, X_2, \ldots) = E_{cs} + \sum_m H_{mm} X_m$$
$$+ \frac{1}{2}\sum_{m,n} H_{mmnn}X_m X_n, \tag{20}$$

where X_m is the square of the m-th orbital rotation parameter. Minimization of Eq. (20) leads to a linear system of equations

$$\mathbf{AX} = \mathbf{b}, \tag{21}$$

where $\mathbf{A}_{mn} = H_{mmnn}$ and $\mathbf{b}_m = H_{mm}$. The solution of this (generally small) system of equations yields the squares of the rotational parameters defining the minimum. There are in general 2^K equivalent solutions if there are K instabilities (negative eigenvalues of the orbital Hessian). An example where Eq. (21) has an acceptable solution is nitrobenzene, shown in Sec. IV.

Only non-negative solutions of Eq. (21) are physically meaningful. For a single triplet instability, X is always positive

TABLE III. The four smallest instability eigenvalues of all-*trans* butadiene, hexatriene, and octatetraene calculated with def2-TZVP basis set.

Butadiene	Hexatriene	Octatetraene
−0.032 69	−0.051 35	−0.062 89
0.042 35	0.011 30	−0.010 61
0.264 69	0.059 61	0.036 14
0.266 99	0.251 98	0.068 68

TABLE IV. The largest singular values of the Hessian eigenvectors in matrix form corresponding to negative instability eigenvalues in Table III.

		Octatetraene	
Butadiene	Hexatriene	1st eigenvector	2nd eigenvector
0.891 33	0.851 60	0.821 23	0.679 13
0.429 21	0.399 50	0.411 56	0.640 84
0.071 21	0.309 31	0.275 15	0.240 52
0.065 83	0.062 43	0.249 15	0.222 34
0.063 22	0.053 54	0.055 53	0.060 90

if the quartic derivative, Eq. (14), is positive. We have not encountered a case with a negative diagonal quartic derivative yet, and a comparison of Eqs. (12) and (14) suggests that if there is an instability, i.e., $\partial^2 E/\partial s^2 < 0$, the diagonal fourth derivative will be positive, although we have not found a general proof. However, for more than one instability, a negative value for some components of **X** is a possibility. An example (ozone) will be shown in Sec. IV. The formal solution of Eq. (18) cannot be used in such cases. Instead, we should consider that there are stationary points on the energy surface when an orbital rotation parameter is zero because, if $X = s^2$, $\partial E/\partial s = 2s (\partial E/\partial X) = 0$ if $s = 0$. One has to try setting all possible combinations of the orbital rotation angles to zero, determine the stationary points under these conditions, and select the minima belonging to positive values of the squared coordinates. They give distinct UHF solutions but generally the lowest one is of interest.

IV. EXAMPLES

Molecular geometries (with constraints in some cases, and with the exception of Cr_2) were optimized at the BP86/def2-TZVP density functional level [32–34] using the PQS software package,[35] and are given in Table S1 of the supplementary material. Instabilities involve primarily valence-type orbitals, and are therefore not very sensitive to the basis set quality beyond a modest level, say split-valence with polarization. Table I compares the negative eigenvalues of the triplet instability matrix for ozone, nitrobenzene, and Cr_2 (the latter at R(Cr−Cr) = 1.68 Å) calculated using the m6-31G* and the def2-TZVP basis sets. (The m6-31G underlying basis set was used for first-row transition metals because the 6-31G basis is severely deficient for these elements,[36] particularly for late transition metals like iron, cobalt, nickel, and copper due to the lack of an important diffuse d orbital; it is identical to the 6-31G basis for main group elements.) Table I shows that the eigenvalues of the electronic Hessian are quite similar for a large basis and a modest 6-31G* basis for a variety of systems.

In Table II, instability eigenvalues and the corresponding singular values are listed for typical aromatic molecules: benzene, naphthalene, and nitrobenzene. In the case of benzene, there is only one negative instability eigenvalue. Fig. 1 shows the orbital pairs corresponding to the three principal components of the instability eigenvector (the elements of the diagonal matrix **D** in Eq. (4)). Although there is only one instability, it has 3 important excitations, all in a conceptual minimum π space. The case is similar for naphthalene: one negative instability vector can be decomposed into 5 orbital pairs, as expected. In nitrobenzene, there are 2 instabilities, one in the nitro group and one in the benzene ring. The main singular values of the second instability eigenvector are similar to the corresponding values in benzene. Fig. S3 of the supplementary material shows the corresponding orbital pairs. Similar calculations were carried out for ferrocene and nickel-porphine; the results are shown in the supplementary material.
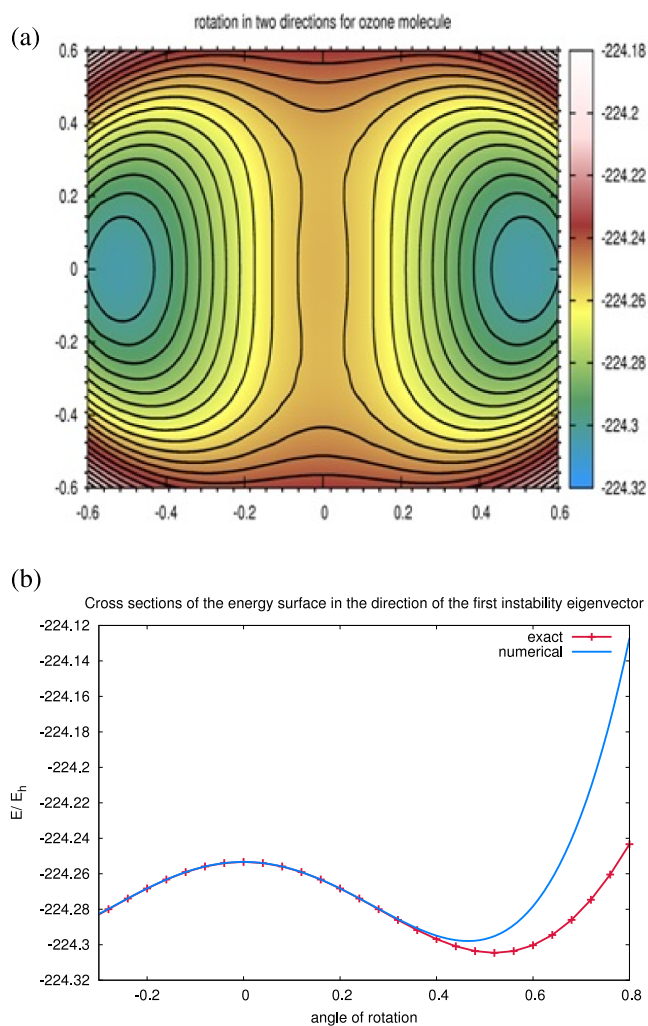

FIG. 2. ((a), top) Contour plot of the UHF energy of ozone (6-31G* basis) as a function of orbital rotations along the largest negative eigenvalue of the instability matrix (x coordinate) and the second eigenvalue (y). Angles in radians, and energy in atomic units (E_h). The minimum on the UHF energy surface lies at $x = \pm0.520$, $y = 0$; the solution of the fourth-order equation gives (±0.465, 0). ((b), bottom) Comparison of the UHF energy (red) with a quartic approximation (blue) for rotations along the largest negative eigenvalue.
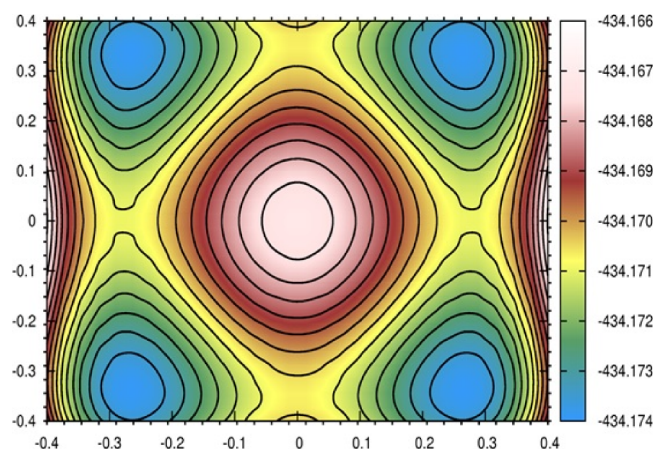

FIG. 3. Contour plot for the UHF energy of nitrobenzene (6-31G*) as a function of the orbital rotation parameters belonging to the largest and second largest negative instability eigenvalues (x and y coordinates, respectively). See Table I. Angles in radians, and energy in atomic units (E_h).

Table III shows the lowest eigenvalues of the electronic Hessian for the first three linear all-E conjugated polyenes, and Table IV gives the major excitations (the largest elements in the matrix **D**, Eq. (4)) for these eigenvalues. There is a clear break between the large (>0.2) and small (~0.05) components. The orbitals span the valence π space and have 2, 3, and 4 important components for butadiene, hexatriene, and octatetraene, as expected. Octatetraene has two instabilities but they span almost the same space. Solving Eq. (21) in the two-dimensional space of squared orbital rotations gives an inadmissible negative solution; the correct solution is $s = 0.5435$ and $t = 0$, i.e., there is only one relevant orbital rotation, and it is along the largest negative eigenvalue. This is the case also for ozone. Fig. 2(a) displays the contour plot of the UHF energy as a function of the orbital rotations for ozone to fourth order; Fig. 2(b) compares the UHF energy with the quartic approximation along the most negative instability eigenvector. A qualitatively different picture is obtained for nitrobenzene. In this molecule, there are two kinds of strong correlation, in the nitro group and in the aromatic ring, as shown in Table II. These are not strongly coupled, and the solution of Eq. (21) gives real solutions for the rotational

FIG. 5. Energy in UHF iteration for nitrobenzene starting from the solution of Eq. (21) (blue) and starting from mixing canonical orbital pairs (red and yellow). The UHF iteration started after mixing the HOMO and LUMO orbitals converges to the RHF energy. Mixing π orbitals on the benzene ring leads to lower energy, but it is still not the absolute minima.

parameters (s, t). A contour plot of the UHF energy $E(s, t)$ as a function of the rotational parameters is shown in Fig. 3. Fig. 4 compares the number of iterations needed to converge the UHF wavefunction for octatetraene, starting with the solution of Eq. (21) versus starting with mixing the HOMO and the LUMO by 30°. In this easy case, the HOMO-LUMO mixing gives leads to the correct solution. Starting with a qualitatively correct wavefunction not only speeds up convergence but also assures us that the correct minimum energy solution was obtained. This is shown in Fig. 5 for nitrobenzene and in Fig. 6 for nickel porphine. Starting the calculations with orbital mixing leads to convergence to a higher energy saddle point on the UHF energy surface for these molecules. Nickel porphine is similar to nitrobenzene in that there are several types of strong correlation. There are 5 negative instability eigenvalues, the first three correspond to correlation among the d electrons on nickel, the last two correspond to correlation among the π electrons in the porphine ring. The
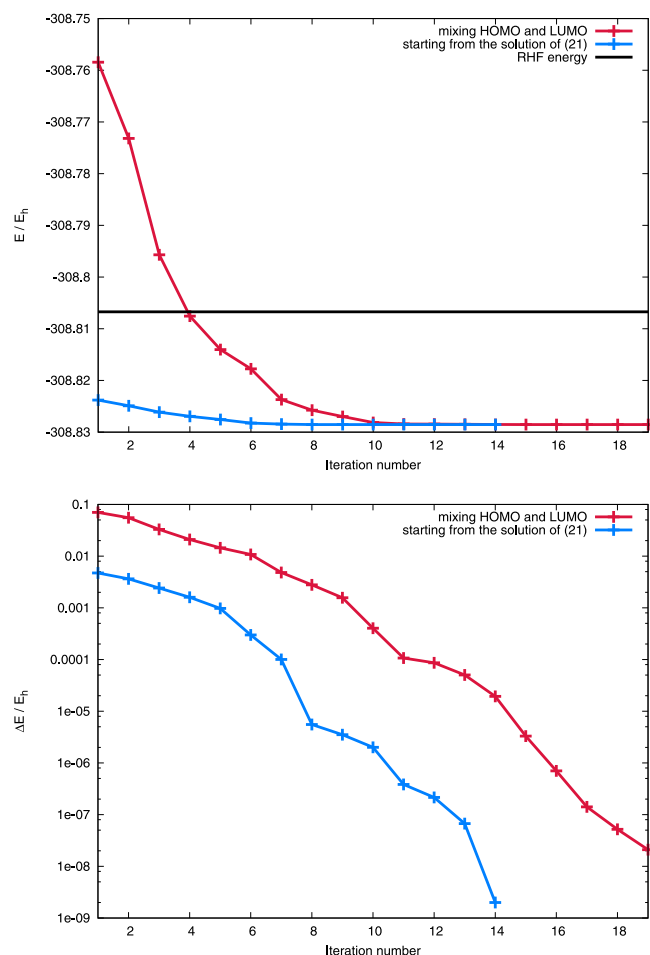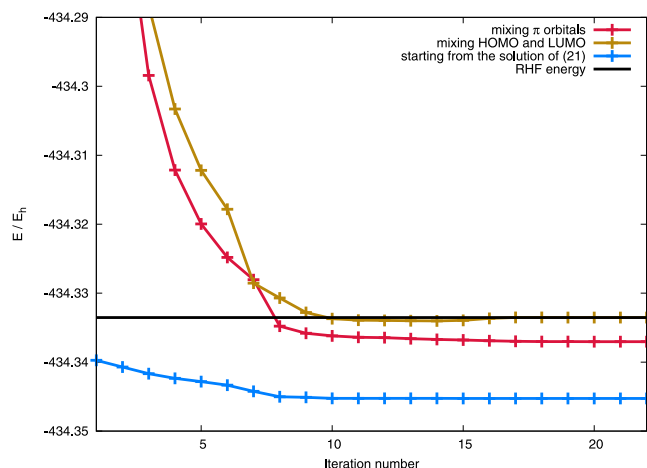

FIG. 4. Energy and energy error in UHF iteration for octatetraene starting from the solution of Eq. (19) (blue) and starting from mixing the HOMO and LUMO orbitals by 30° (red). In this simple case, mixing the HOMO and LUMO orbitals provides a suitable starting point. Starting from the solution of Eq. (20) enhances the convergence.
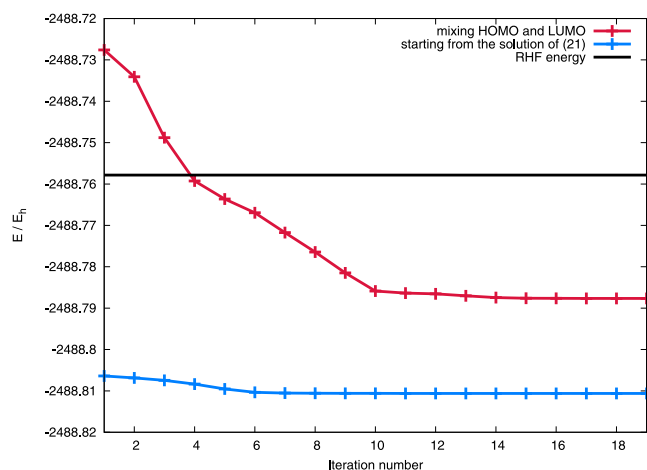

FIG. 6. UHF energy for Ni-porphine as a function of the SCF iteration number, starting from the solution of Eq. (21) (blue) and starting from mixing the HOMO and LUMO orbitals by 30° (red). The UHF procedure for the latter calculation converges but not to the absolute minimum.

positive solution of Eq. (21) lies in the subspace spanned by eigenvectors 1, 4, and 5. The UHF energy with this starting solution is only about 4 mE$_h$ above the converged value (Fig. 6). Further examples with orbital plots, for instance, for permanganate, m-benzyne, and nickel-salen (a model of Jacobsen's catalyst) are provided in the supplementary material. The case of m-benzyne deserves a comment. Starting the UHF iteration by mixing the HOMO and the LUMO gives a solution with only one significantly split orbital pair (see the caption of Fig. S4 of the supplementary material), corresponding to the bonding and antibonding σ orbitals of the largely broken C$_1$−C$_3$ bond. Using our method leads to a slightly (0.4 mE$_h$) lower UHF energy with eight fractionally occupied orbital pairs in the 0.005-1.995 range. Two of these belong to the C$_1$−C$_3$ σ bond, the other 3 pairs describe weaker static correlation in the aromatic π space. The solution obtained from the HOMO-LUMO mixing is a saddle point.

V. CONCLUSIONS AND OUTLOOK

We have revisited the determination of broken spin-symmetry unrestricted Hartree-Fock (UHF) wavefunctions in even-electron systems, starting from the closed shell restricted Hartree-Fock (RHF) solution. This is needed for the automatic determination of the active space for strong correlation as the space of the fractionally occupied UHF charge natural orbitals. It is well known that the RHF wavefunction is triplet unstable if the RHF electronic Hessian has at least one negative eigenvalue. We have shown that the quartic power series expansion of the UHF energy as a function of the orbital mixing parameters s and t does not have terms like s^3t or st^3 *in the basis of the eigenvectors of the orbital Hessian*. This result can be generalized to higher (for instance 6th degree) powers, e.g., terms which contain odd powers like s^5t, s^3t^3, etc., vanish in the eigenvector basis. However, a quartic expansion is sufficient in essentially all cases. The vanishing of terms which contain odd powers in individual orbital rotation parameters is not a symmetry property (symmetry only ensures that the overall power must be even), but a consequence that these terms are proportional to the quadratic term H_{st} which is zero in the eigenvector basis.

Due to this surprising and lucky coincidence, the squares of orbital rotation parameters defining the UHF energy minimum can be determined in fourth order simply by solving a linear system of equations, without iteration, subject to the condition that the solution is positive. Some orbital rotations need to be set to zero if negative solutions are obtained. Our method eliminates the uncertain search for a UHF solution, which frequently yields a saddle point and not the absolute minimum. We have evaluated the quartic derivatives numerically, but analytical formulas which have a slight advantage were also derived.

Our method can be generalized to 6th (and even 8th) degree expansions. In these cases, the solution must be determined iteratively. The computational cost of this is negligible. Generalizing our results to complex instability, which behave very similarly to triplet instability,

is straightforward. Further generalizations are possible to systems with unpaired electrons, and general (non-collinear) spins. Application to density functional theory would be probably of the greatest practical value. DFT is much less prone to triplet instability than Hartree-Fock theory because a significant part of electron correlation is included in DFT. We are considering a generalization to systems with a net spin for both Hartree-Fock and DFT calculations.

SUPPLEMENTARY MATERIAL

Molecular geometries and tables of orbital Hessian eigenvalues and their singular value decompositions for m-benzyne, ferrocene, Ni-porphine, permanganate, and nickel-salen (a model of Jacobsen's catalyst), orbital plots for nitrobenzene and Ni-porphine, and SCF convergence behavior for m-benzyne are provided in the supplementary material.

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