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Alex J. W. Thom[1,a)] and Martin Head-Gordon[1,2]

[1]*Department of Chemistry, University of California Berkeley, California 94720, USA*
[2]*Chemical Sciences Division, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA*

Using the method of self-consistent field metadynamics, we locate some of the low-energy solutions to the Hartree–Fock (HF) equations on LiF and O_3. The located solutions qualitatively resemble the adiabatic electronic states in these systems. We formulate the method of nonorthogonal Configuration Interaction (CI) to interact these solutions with cubic scaling with system size and quadratic scaling with the number of solutions. The resultant solutions display the avoided crossings and, in O_3, a conical intersection expected of the adiabatic states. In LiF the relevant solutions coalesce and disappear from Unrestricted HF space indicating a more general HF theory is required. © *2009 American Institute of Physics*. [doi:10.1063/1.3236841]

We have recently reported the method of self-consistent field (SCF) metadynamics,[1] which enables multiple solutions to the SCF equations (the stationary values of the energy as a function of the electron density) to be found with relative ease, in particular, locating excited solutions to the SCF equations, and in some cases lower energy solutions. An obvious extension to this is to pose the question: "Do the excited solutions to the SCF equations have any physical meaning?" While the variational principle gives good justification for using the lowest energy solution of the SCF equations as an approximation to the ground state wave function, we do not know of any such reasoning to justify the use of excited solutions as approximations to excited states. Gilbert and co-workers[2,3] performed a number of studies on the excited solutions and showed that they provide relatively good values of vertical excitation energies. In contrast, there has been much speculation about the quality of the excited states produced by time-dependent density functional theory (see, e.g., Refs. 4 and 5), with qualitative deficiencies noted in its ability to describe conical intersections.[6]

In this paper we locate some of the low-energy SCF solutions for the LiF and O_3 molecules, and note that they have very similar properties to the diabatic electronic states of the molecules. In particular the SCF solutions are not subject to noncrossing rules, and do in fact often cross each other. We further have seen that the states maintain essentially the same electronic structure during changes in the atomic positions, behaving therefore in a quasidiabatic fashion.

We shall focus on the solutions to the Hartree–Fock (HF) equations in this paper. Such states form a natural basis for a configuration interaction calculation between them to produce adiabatic states.[7] These adiabatic states behave in a qualitatively similar fashion to those produced from the more complicated multiconfigurational SCF (MCSCF) treatments, producing avoided crossings and conical intersections. In ad-

dition, as they are formed from a basis of size-consistent SCF solutions, the states should maintain size consistency.

Interaction of the SCF solutions is complicated by the lack of orthogonality between the canonical orbitals of different solutions.[8] Working in a basis, typically of atomic-centered Gaussians, $|\chi_\mu\rangle$, in a similar manner to a number of past nonorthogonal CI (NOCI) approaches,[9] we calculate the Hamiltonian matrix elements. Using Löwdin's pairing theorem,[10,11] for each pair of solutions, we transform the orbitals of each solution to be biorthogonal, rather than the more complicated adjoint-based methods.[12,13]

For solutions w and x with wave functions $|{}^w\Psi\rangle$ and $|{}^x\Psi\rangle$ formed as Slater determinants from the n canonical occupied orbitals $|{}^w\phi_i\rangle$ and $|{}^x\phi_i\rangle$, respectively, we use the pairing method to create, by a unitary transformation, sets $|{}^w\widetilde{\phi}_i\rangle = \Sigma_\mu |\chi_\mu\rangle {}^x\widetilde{C}^\mu_{\cdot i}$ and $|{}^x\widetilde{\phi}_i\rangle = \Sigma_\mu |\chi_\mu\rangle {}^x\widetilde{C}^\mu_{\cdot i}$ which satisfy

$$\langle {}^w\widetilde{\phi}_i | {}^w\widetilde{\phi}_j\rangle = s_i \delta_{ij}, \tag{1}$$

where $0 \le s_i \le 1$ and δ_{ij} is diagonal. This process involves a diagonalization of the overlap matrix between sets of orbitals, and thus scales as $\mathcal{O}(n^3)$ for each pair of solutions. The overlap between the determinants is given by the product of orbital overlaps, $S = \Pi_i s_i$. As when calculating matrix elements between Slater determinants formed from the same set of orthogonal orbitals, it is convenient to classify pairs of solutions based on the number of zeros in the set $\{s_i\}$ for that pair. We also create a reduced overlap which excludes the zero values,

$$\widetilde{S} = \prod_{\substack{i \\ s_i \ne 0}} s_i. \tag{2}$$

If there are more than two zeros in $\{s_i\}$, the Hamiltonian matrix element between the two SCF solutions will be zero as the Hamiltonian is a two-electron operator. Otherwise, the generalized Slater–Condon rules (Table I) can be used to calculate the matrices $H_{wx} = \langle {}^w\Psi | \hat{H} | {}^x\Psi\rangle$ and $S_{wx} = \langle {}^w\Psi | {}^x\Psi\rangle$.

a)Electronic mail: alex.thom@berkeley.edu.

TABLE I. The generalized Slater–Condon rules for a biorthogonal basis $\langle^w\tilde{\phi}_i|$ and $|^x\tilde{\phi}_i\rangle$ defined by Eq. (1), corresponding to nonorthogonal SCF solutions w and x. h_{ii} and $\langle ij\|ij\rangle$ are one- and two-electron integrals transformed into this basis. Superscripts α and β represent summations over orbitals of only that spin. σ_i is the spin of orbital i. $J[P]$ and $K[P]$ indicate Coulomb and exchange matrices made by contraction of matrix P with the four-index electron repulsion integrals. $\tilde{S}$ is the reduced overlap defined in Eq. (2).

Zeros in $\{s_i\}$	Contribution	Matrix form
None	$\left(\frac{1}{2}\Sigma_{i,j}\frac{\langle ij\|ij\rangle}{s_i s_j}+\Sigma_i\frac{h_{ii}}{s_i}\right)\tilde{S}$	$\left(\frac{1}{2}{}^{wx}W\cdot J[^{wx}W]+{}^{wx}W^\alpha\cdot K[^{wx}W^\alpha]+{}^{wx}W^\beta\cdot K[^{wx}W^\beta]+\Sigma_i\frac{h_{ii}}{s_i}\right)\tilde{S}$
s_i	$\left(\Sigma_j\frac{\langle ij\|ij\rangle}{s_j}+h_{ii}\right)\tilde{S}$	$({}^{wx}P_i\cdot J[^{wx}W]+{}^{wx}P_i\cdot K[^{wx}W^{\sigma_i}]+h_{ii})\tilde{S}$
s_i, s_j	$\langle ij\|ij\rangle\tilde{S}$	$({}^{wx}P_i\cdot J[^{wx}P_i]+{}^{wx}P_i\cdot K[^{wx}P^{\sigma_i}])\tilde{S}$
>2	0	0

Through the use of unweighted and weighted codensity matrices,

$${}^{wx}P_i^{\mu\nu} = {}^w\tilde{C}_{\cdot i}^\mu \cdot {}^x\tilde{C}_i^{*\nu}, \tag{3}$$

$${}^{wx}W^{\mu\nu} = \sum_i \frac{{}^{wx}P_i^{\mu\nu}}{s_i}, \tag{4}$$

each matrix element requires a Coulomb and exchange matrix build, resulting in a scaling of $\mathcal{O}(N^2)$ for each element, where N is the size of the atomic orbital basis.

The solutions of the generalized eigenvalue problem,

$$\sum_x H_{wx}D_{xi} = \sum_x S_{wx}D_{xi}E_i, \tag{5}$$

are the adiabatic wave functions $|\Psi_i\rangle=\Sigma_x|^x\Psi\rangle D_{xi}$ with energy E_i. The most computationally expensive steps in this method are the diagonalization of the overlap matrix between orbitals of each solution, which scales as n^3, and the calculation of an exchange matrix for each Hamiltonian matrix element required. This makes the overall scaling of this method is $\mathcal{O}(n_s^2 \max(n^3, N^2))$, where n_s is the number of SCF solutions used, making it applicable to even very large systems.

To analyze solutions it is convenient to define a distance metric between them, and we choose that used in SCF meta-dynamics,

$$d_{wx}^2 = n - {}^wP^{\mu\nu}\cdot{}^xP_{\nu\mu}, \tag{6}$$

where $^xP_{\mu\nu}=S_{\mu\sigma}{}^xP^{\sigma\tau}S_{\tau\nu}$ is the covariant density matrix, and $^xP^{\mu\nu}$ and $S_{\mu\nu}$ are the conventional contravariant density and covariant overlap matrices, all expressed in the nonorthogonal atomic orbital basis $|\chi_\mu\rangle$. The metric is bounded by 0 and n, the number of electrons in the system, and degenerate solutions may be differentiated by the nonzero distance between them. This metric can also be used between solutions at different geometries and although the metric no longer has the same bounds, the distance between solutions is a continuous function of molecular geometry, enabling solutions to be traced through nuclear coordinate space.

We turn first to the molecule LiF, which is known to have an avoided crossing in its dissociation curve.[14–16] At equilibrium the structure is covalently bound, but heavily polarized toward Li$^+$ F$^-$; but as the ionization potential of Li is greater than the electron affinity of F, the molecule disso-

ciates to neutral atoms. The two diabatic states corresponding to these different electronic configurations cross and the interaction between them results in the avoided crossing.

In Fig. 1 we show the lowest unrestricted Hartree–Fock (UHF) solutions in a 6-31(2+,2+)G** basis, corresponding to these two states. The distance between the states varies between 1.06 and 1.09 electrons over the curve, confirming they are indeed distinct. The lower solution at equilibrium is a restricted Hartree–Fock (RHF) solution, which remains a local UHF minimum throughout the curve, and is of $^1\Sigma^+$ symmetry.

The higher solution shown at equilibrium is strictly UHF and multiply degenerates, corresponding to the two different arrangements of atomic spin populations, as well as an orbital angular momentum degeneracy, making it a Π state. This degenerate set of UHF solutions is heavily spin contaminated with $\langle\hat{S}^2\rangle\approx 1$. Configuration interaction between these two degenerate states produces both $^1\Pi$ and $^3\Pi$, which are essentially degenerate, in the manner of the half-projected HF method.[17–19] Symmetry considerations make the crossing of these states with the lower state an allowed crossing, and they do indeed cross.

The avoided crossing occurs between $^1\Sigma^+$ states. Plotted inset in Fig. 1 are the two next lowest Σ^+ states that we have located, and it can be seen that they coalesce at a bond length of 3.15 Å. Once again they are heavily spin contaminated and exist as spin-flipped pairs. One of these solutions is the UHF ground state at >3.6 Å.
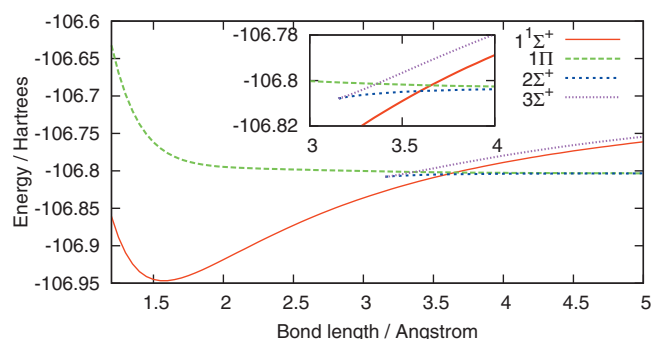

FIG. 1. The dissociation of LiF in UHF. The ground state $^1\Sigma^+$ (solid red) dissociates to Li$^+$F$^-$. $^1\Pi$ and $^3\Pi$ states are close to degenerate (long dash green) and dissociate to neutral Li and F. Inset: two Σ^+ solutions (short dash blue and dotted purple) coalesce and disappear.
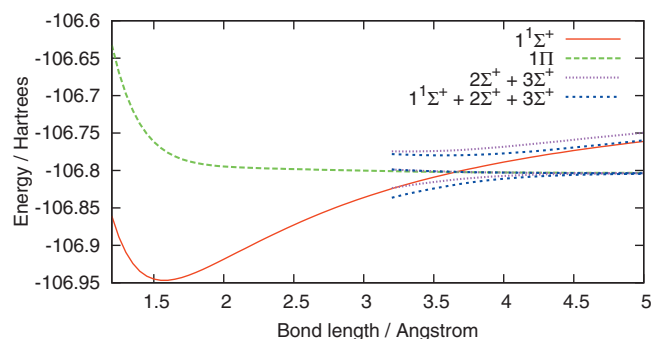
FIG. 2. The result of CI between the lowest Σ^+ states of LiF. These have been labeled according to their energy order at 3.5 Å. The + in the key indicates inclusion in the CI. The $2\Sigma^+$ and $3\Sigma^+$ excited SCF states exist in spin-flipped UHF pairs, and both spin-flipped configurations have been included in the CI. Coupling of $2\Sigma^++3\Sigma^+$ results in an avoided crossing of singlet states and a triplet state nearly degenerate with the 1Π state. The remaining triplet state resulting from this is much higher in energy and has been omitted.

The coalescence of these solutions causes significant problems in the CI, however, as the $^1\Sigma^+$ and $^3\Sigma^+$ solutions created through interaction end abruptly, and so are unsuitable for interaction with the lowest solution, as this leads to a discontinuous binding curve where the solutions vanish. The CI interactions between the Σ^+ states are shown in Fig. 2. While an avoided crossing is seen, the coalescence of solutions in UHF means it cannot be fully followed at present. We find this coalescence an extremely interesting phenomenon. With excited states, unlike the ground state, there are no guarantees that a continuous solution exists over changes in geometry within a version of HF theory with the restrictions of real orbitals or the same orbitals for different spins (RHF theory). We believe that to remedy this situation it will be necessary to follow the solutions into the complex and/or generalized HF space[20] to retain continuous solutions for interaction. As these solutions are the lowest UHF solutions at bond lengths >3.6 Å, they cannot be easily ignored and it is likely that such problematic solutions exist in many other molecules.

We next turn to the molecule O_3, whose potential energy surface has well studied using MCSCF theories (see Ref. 21 and references therein), and a conical intersection located between the lowest two adiabatic surfaces. Constraining our investigation to the C_{2v} subspace using RHF theory in a Dunning cc-pVTZ basis,[22] there are two significant minima: The ground state is an open geometry and the higher lying state is a closed D_{3d} equilateral triangle structure (Fig. 3). The two minima have different electronic structures and are located on different SCF surfaces. The electronic structure of each SCF surface remains approximately constant (as evinced by an analysis of the localized orbitals[23]), and they intersect at an intermediate geometry; this seam of intersection follows a roughly fixed O–O–O angle of about 89°. Around this seam, there are two further low-energy excited solutions, shown in Fig. 4.

NOCI of two lowest solutions results in an avoided crossing along the whole seam, giving rise to a ridge along the location of the seam. This is an example of the *weak noncrossing rule*. Atchity and co-workers[26,27] showed that
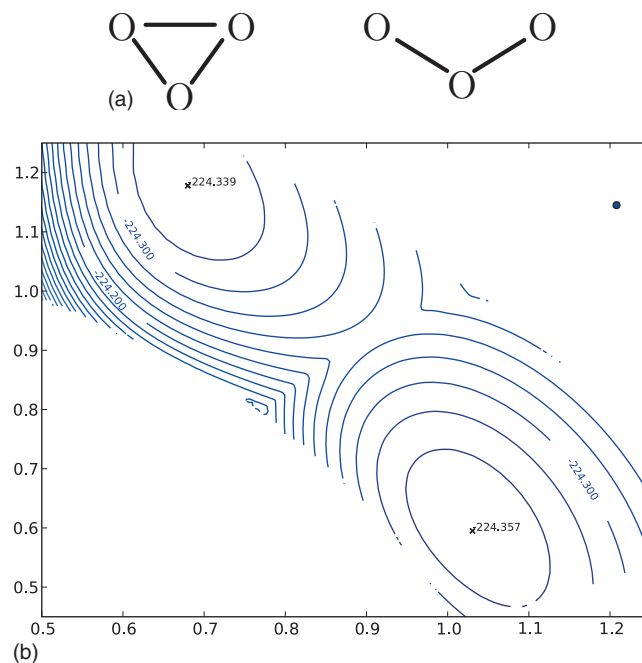

FIG. 3. The lowest RHF energy in O_3. Axes show (x,y) meaning atoms at (x,y), $(0,0)$, and $(-x,y)$. The surface is formed by the intersection of the two lowest SCF surfaces and has a sharp ridge. Above the plots is the electronic structure at the relevant minima, showing the bonding orbitals with all other orbitals fully localizable. A cross denotes a SCF minimum in either of these two states and a filled circle denotes the location of the conical intersection.

this occurs because the coupling matrix element between the solutions is given by a Coulomb interaction which can never be negative. In our nonorthogonal framework, this is not strictly true, but the coupling element does remain nonzero along the degenerate seam (Fig. 5).

The inclusion of higher solutions, which amount to adding some nondynamical correlation relaxes these restrictions and an intersection appears on the ridge. Plotting the open solution component of the lowest wave function for circumnavigations in the vicinity of the intersection (Fig. 6) shows a distinctive phase change when the intersection point is within the circuit, and so we can deduce the existence of a conical intersection.

We end these investigations with a note of caution, however. While the interaction of SCF solutions produces qualitatively physical results, it is not a black-box process. In
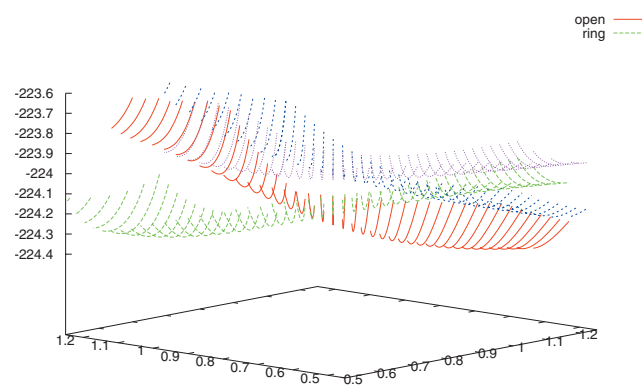

FIG. 4. Three dimensional surface plot of the four surfaces considered in O_3 NOCI. The coordinates are as in Fig. 3.
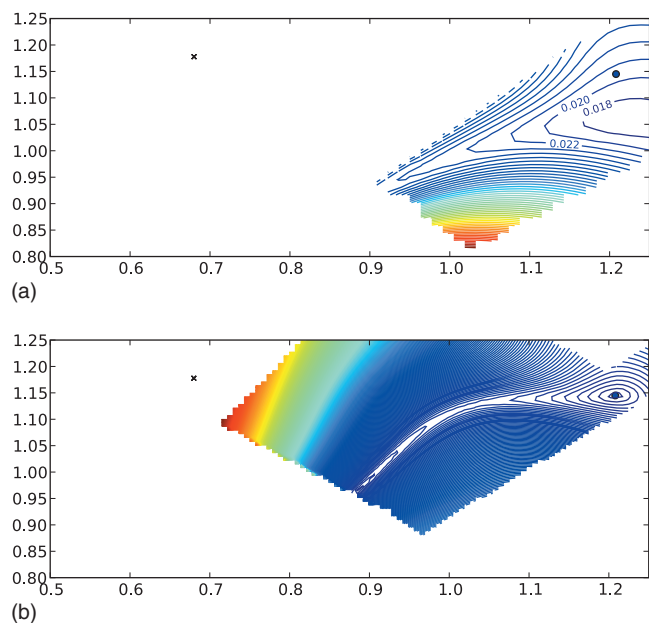
FIG. 5. Contour plots of the energy difference (in E_h) between the lowest two O_3 NOCI solutions based on: two states (upper)—no conical intersection is seen and adiabatic states are always separated by more than 0.016 E_h; four states (lower)—a conical intersection is seen (as marked by the blue dot). The contours in the lower plot are at 0.001 E_h.

particular, care must be taken in the selection of the SCF solutions. Figure 1 shows that in the region of the avoided crossing in LiF, different SCF solutions are in fact the lowest energy states. As the bond distance is decreased, these solutions coalesce with other SCF solutions and disappear from UHF space. We believe that they are likely to exist in complex or generalized HF spaces beyond this point. The inclusion of these states in the CI calculations leads to discontinuities and unphysical behavior when they disappear, and so we have excluded them from our consideration. In O_3, a pair of lower energy broken-symmetry RHF solutions breaks off from the open structure solution in the vicinity of the conical intersection; they have not been considered as their inclusion also leads to discontinuities. The nature and location of such coalescing solutions, including their extension into more general HF spaces, is a topic of active research.

In conclusion, we have studied some of the low-energy SCF solutions of LiF and O_3, located using the technique of
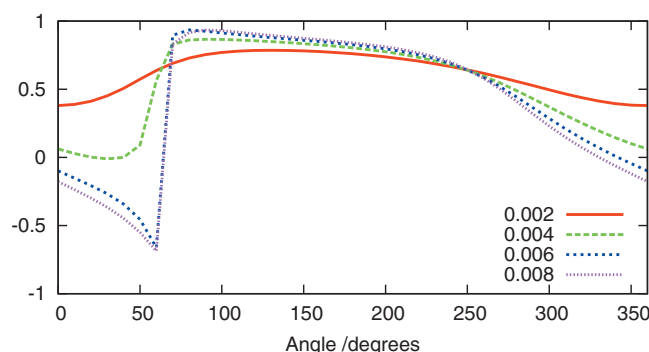

FIG. 6. The component of the open solution in the four-state NOCI. The scans are circular and radiate from a point close to the conical intersection, the key showing the radius of the scan in Å. When the conical intersection is encompassed, there is a clear Berry phase change (Refs. 24 and 25).

SCF metadynamics, and find them to qualitatively resemble the low-energy diabatic states in these systems. Using the method of nonorthogonal configuration interaction between different SCF solutions, we have been able to recover adiabatic states with avoided crossings and a conical intersection in ozone. In LiF we see that some of the relevant SCF states coalesce and disappear from UHF space making the solutions of the CI discontinuous in this space, and indicating a more general HF theory may be required. This method has an extremely favorable scaling and may be used in cases where multiconfigurational SCF procedures are prohibitively expensive.

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