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The constrained density functional theory–configuration interaction (CDFT-CI) method has previously been used to calculate ground-state energies and barrier heights. In this work, it is examined for use in computing electronic excited states, for the challenging case of conical intersections. Conical intersections are a prevalent feature of excited electronic surfaces, but conventional time-dependent density functional theory calculations are found to be entirely unsatisfactory at describing them, for two small systems. CDFT-CI calculations on those systems are found to be in qualitative agreement with reference CAS surfaces. These results suggest that with a suitable definition of atomic populations and a careful choice of constrained states, CDFT-CI could be the basis for a seamless description of electronic degeneracy. © *2010 American Institute of Physics*. [doi:10.1063/1.3470106]

Time-dependent density functional theory (TD-DFT) is now well-established as an efficient method to calculate excited-state energies of many chemical systems, being frequently used to investigate photochemistry and to compute vertical excitation energies.[1–4] The manifold of ground and excited electronic states for almost all molecular systems is rife with conical intersections (CIs)—seams of true degeneracy between electronic states. These intersections are frequently important for photochemical dynamics, as an intersection provides an easy pathway for nonradiative decay, and CIs are usually quite accessible to photoexcited systems.[5] Even on the ground electronic state, and even in cases where the actual intersection is not energetically accessible, CIs can still have a dramatic effect on quantum dynamics, as evidenced in the phenomenon of geometric phase.[5] Over the entire many-dimensional manifold of states, CIs are actually quite prevalent, and accurate excited-state or dynamics treatments must account for them.[5] Unfortunately, despite its many successes, TD-DFT completely fails to describe conical intersections between excited states and the ground state.[6] In most cases, TD-DFT only produces one direction of degeneracy-splitting, and the S_1 state frequently has an ill-behaved $\partial E / \partial R$ in the vicinity of the intersection.[6] In order to get a qualitatively correct treatment of CIs, multireference methods such as complete active space (CAS), multireference configuration interaction (MRCI), and CASPT2 must be used.[6] Unfortunately, existing multireference treatments are almost universally wave function-based, and the computationally reasonable methods (such as CAS) have been shown to give only qualitatively correct descriptions of multistate energy-surface manifolds;[7] more accurate methods such as MRCI are frequently too expensive for use on real systems. We have developed a multireference DFT method, constrained density functional theory–configuration interaction (CDFT-CI), in previous works;[8,9] it has been shown to

be effective at calculating ground-state energies and barrier heights,[10] but its treatment of electronic excited states has yet to be presented. In this Communication, we present CDFT-CI as a method for obtaining qualitatively correct energy-surface manifolds encompassing both ground and excited electronic states, producing well-behaved conical intersections at appropriate geometries.

CDFT-CI is designed to be a DFT-based method that can robustly treat systems with both dynamic and static correlation. Existing DFT functionals can perform well for systems with dynamic correlation, but tend to do poorly when static correlation is present (such as when multiple near-degenerate states are accessible).[11–14] Other techniques combining DFT with configuration interaction have been proposed;[15] these and other related techniques are discussed in relation to CDFT-CI in our previous work.[9,10] CDFT-CI works by introducing an active space whose states originate from distinct (constrained) SCF calculations, constructing a CI matrix of fully *ab initio* energies and couplings, and diagonalizing that matrix to obtain energies and coefficient vectors for the adiabatic states. This explicitly includes static correlation due to the multireference nature of the eigenstates, and dynamic correlation is treated through the DFT functional used in the formation of the basis states. In particular, these states are produced using the constrained DFT (CDFT) method, which introduces an additional constraint potential to each state's Hamiltonian, enforcing a charge or spin constraint on some subset of the system of interest.[16] The CDFT equations rely on a partitioning of the system into multiple fragments and a means for assigning (spin) density to individual atoms.[16]

For each state i in the CDFT-CI active space, one minimizes the DFT energy subject to the constraint that the average spin and charge on each fragment take on the values specified for that state/fragment pair. The CDFT algorithm enforces the constraint by applying a potential, $\hat{V}_i(\vec{r})$, to the system. A more detailed description of the working equations is presented in Refs. 16 and 8.

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We take the time to note that the integer constraints that we might naïvely apply to molecular fragments from our chemical intuition (e.g., $N = \pm 1$ and $S = \frac{1}{2}$) are not always reasonable. This can be due to charge- or spin-localized states that are inherently diffuse, or just to the inability of the charge model to describe bonded systems. (We recall that the notion of atomic charge within a molecular system is not well-defined, so we inherently must use an arbitrary scheme.[17]) This leads to a need to modify the given (intuitive) constraint values to account for the contribution to the computed "charge" on one fragment from the density tails of other fragments. This is accomplished by means of a "promolecule" formalism, in which the fragments of the constrained system are treated as independent systems, with integer charge and spin (as prescribed by the integer constraint values). A self-consistent converged density is obtained for each such fragment, and the sum of these fragment densities is integrated against the charge/spin prescription to determine the values of N and S that are used in the final calculation for the constrained state. A more in-depth discussion of the need for modified constraint values may be found in Ref. 9.

Once we have obtained a set of CDFT states (using the corrected N and S), we can then proceed to construct our CI matrix and the corresponding nonorthogonal secular equation,

$$
\begin{pmatrix}
H_{11} & H_{12} & \cdots & H_{1N} \\
H_{21} & H_{22} & & H_{2N} \\
\vdots & & \ddots & \vdots \\
H_{N1} & H_{N2} & \cdots & H_{NN}
\end{pmatrix}
\begin{pmatrix}
c_1 \\ c_2 \\ \vdots \\ c_N
\end{pmatrix}
$$
$$
= E
\begin{pmatrix}
1 & S_{12} & \cdots & S_{1N} \\
S_{21} & 1 & & S_{2N} \\
\vdots & & \ddots & \vdots \\
S_{N1} & S_{N2} & \cdots & 1
\end{pmatrix}
\begin{pmatrix}
c_1 \\ c_2 \\ \vdots \\ c_N
\end{pmatrix}. \quad (1)
$$

The diagonal elements of **H** are just the energies of the constrained states that form the basis for the active space; the off-diagonal elements are constructed as[9,10]

$$
H_{ij} = H_{ji} = \frac{F_i + F_j}{2} S_{ij} - \left\langle \Phi_i \left| \frac{\hat{V}_i + \hat{V}_j}{2} \right| \Phi_j \right\rangle, \quad (2)
$$

where Φ_i is the Kohn–Sham determinant for the ith CDFT state, F_i is the energy of the ith CDFT state in the presence of the constraining potential $\hat{V}_i$, and S_{ij} is just $\langle \Phi_i | \Phi_j \rangle$. In the context of this configuration-interaction calculation, it is very natural to think of the CDFT states as being diabatic states and these H_{12} matrix elements as the diabatic couplings between them. (Note that these couplings as written are computed in a nonorthogonal basis and are only useful in their own right after transformation to an orthogonalized basis; unfortunately, such an orthogonalization does lose some information about the nature of the diabatic states.) The diabatic nature of the states is a consequence of how they are formed—they are explicitly constructed to have charge/spin distributions that are independent of the nuclear configuration.

The CDFT-CI matrix diagonalization thus produces adiabatic states, and we expect that the true character of the ground *and excited* states of the system will be equally well-represented in them. Both ground and excited states arise from the same CI diagonalization and are thus treated on an equal footing. This is in contrast to methods such as TDDFT, which generate an SCF ground state as a reference state and then seek to treat excited states as (single) excitations from that reference.[18,19] Such single-reference calculations are particularly prone to failure in the vicinity of conical intersections, where the nature of the exact ground state changes rapidly in a fashion that is very difficult for DFT methods to reproduce—the procedure for obtaining the DFT ground state has no mechanism to respond to low-lying excited states. Furthermore, the response state essentially can only account for single excitations, and this is frequently insufficient to describe the full conical nature of the intersection.[6] CDFT-CI can fully treat any number of different excitations provided that the appropriate diabatic states are included in the configuration interaction. CDFT-CI may even prove superior to methods such as MR-CISD and CASPT2 in providing a consistent treatment of excited states of different characters, without invoking the extreme computational expense of coupled-cluster calculations.

We have implemented CDFT-CI in a development version of Q-CHEM 3.2;[20] the calculations described in this work were performed using the B3-LYP functional with the cc-pVDZ basis for water and the 6-31G basis for trihydrogen. TD-DFT and CAS calculations were performed using GAUSSIAN 03.[21] For the CDFT calculations underlying the CDFT-CI framework, atomic charges (and thus constraining potentials) were determined by applying Becke's multicenter integration scheme[22] against the (spin) density and attributing the results to the corresponding atomic centers.

The first system we consider is the simplest system to possess a conical intersection—trihydrogen. An intersection is symmetry-constrained to occur at all equilateral triangular geometries; to choose a particular one, we scanned over the symmetric "breathing" mode to find the lowest-energy such state. This was found to be at $R = 1.104$ Å for ground-state B3-LYP, $R = 1.198$ Å for full CI, and $R = 1.336$ Å for CDFT-CI. The well is rather shallow and depends fairly strongly on the size of the basis set. We then held fixed two hydrogens on the y-axis at $\pm R/2$ and scanned over the x- and y-coordinates of the third hydrogen. As shown in Fig. 1, TD-DFT does locate an intersection of electronic states with two splitting coordinates (three such intersections, actually!), but they are offset from the equilateral geometry and, furthermore, are qualitatively incorrect—the upper state at the intersection is not conelike, being instead a sharp cusp. For CDFT-CI, we considered three diabatic states in our CI matrix. In each state, we forced all of the excess spin density to localize on a single H atom; we did this for each H atom in turn. Figure 1 shows how the CDFT-CI surfaces meet in a well-formed dual-lobed cone that mirrors the full CI result.

Like H_3, the water system has only three atoms. However, we now seek an intersection at a (again, symmetry-constrained) linear geometry. Since we know that a seam of conical intersections exists at linear geometries,[23] we can
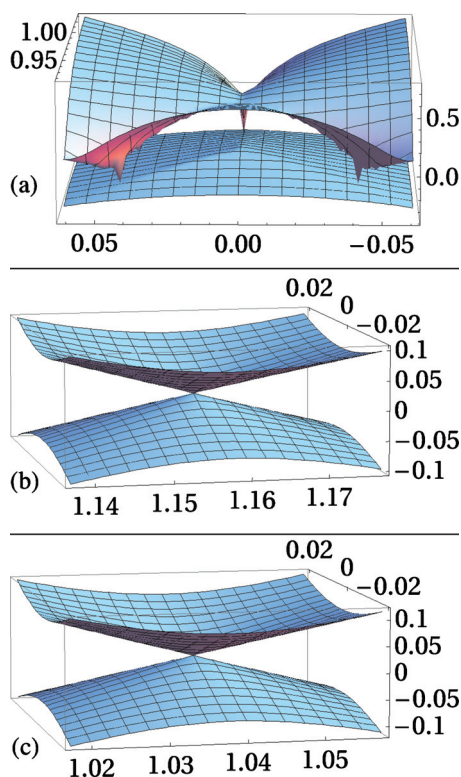
FIG. 1. Triangular trihydrogen energy manifolds, as computed by (a) TD-DFT, (b) CDFT-CI, and (c) full CI. Note the different energy scales for TD-DFT.

FIG. 2. Symmetric water energy manifolds, as computed by (a) TD-DFT, (b) CDFT-CI, and (c) CAS(6,9).

accurately locate an intersection by scanning over symmetric linear geometries; in this case, we find an intersection at $R_{O-H}=1.484$ Å for TD-DFT, $R_{O-H}=1.355$ Å for CAS(6,9), and $R_{O-H}=1.355$ Å for CDFT-CI. Using this geometry as the center for our scans over the internal coordinates for the symmetric stretch and bend, we produce the data plotted in Fig. 2. Clearly, TD-DFT fails to describe the conical intersection, as only one splitting direction is found, instead of the correct two. The excitation energies away from the intersection are also too small (less than 1 eV) for larger R (and $\theta \approx 180°$). The TD-DFT method is not flexible enough to fully describe the excited state in the vicinity of the intersection. For CDFT-CI, in constructing our diabatic basis, we consider an active space of four states; in particular, we can make a covalent state with the oxygen atom a triplet ($S = \pm 1$), which is paired with a triplet "H_2" ($s = \mp 1$). We also include the two ionic states OH^-/H^+ and H^+/OH^- to fill out the four. The CDFT-CI surfaces meet at a well-defined cone and smoothly vary away from the intersection; the comparison with the CAS surfaces is quite favorable.

We note that attaining the correct qualitative behavior does rely on some amount of chemical intuition in the selection of constrained states for the CI matrix. Some preliminary CDFT-CI calculations on water with the ionic states in the active space replaced by states with $S=0$ constraints on both O and H_2 produced a conical intersection at the unphysical R_{O-H} of 0.94 Å! This active-space dependence is similar to the behavior of complete active space wave function methods—a CAS(2,2) calculation on water also finds an intersection in the vicinity of 0.9 Å, whereas CAS(4,4) is in
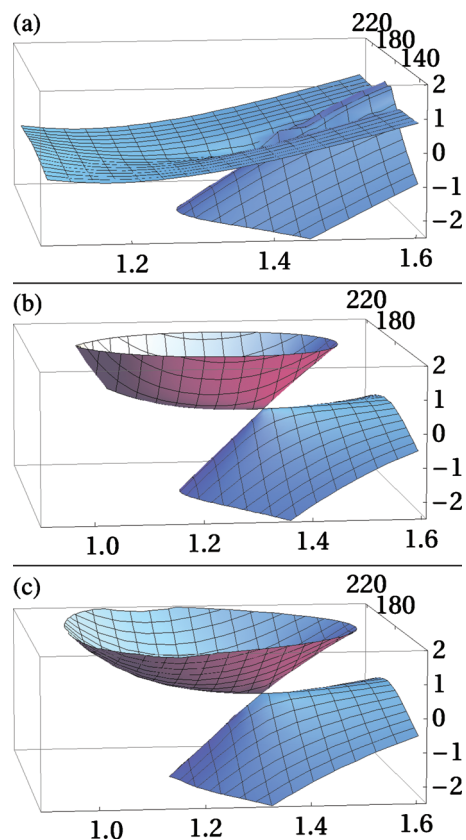
the correct area, near 1.4 Å. Poorly chosen active spaces sometimes fail to yield an intersection at all. Experimentation and/or prior knowledge of the nature of the states of interest is needed in order to perform reliable CDFT-CI calculations, but we expect that to some extent this can be avoided by using a larger active space as can be done with MCSCF. However, large active spaces have not been necessary for the small systems considered in this work.

We find that CDFT-CI is an effective DFT method for computing qualitatively correct excited states even for difficult cases such as the vicinity of conical intersections. This is a dramatic improvement over TD-DFT, which completely fails to give a proper description of the intersection (and thus the surfaces themselves in the vicinity of the intersection). We find this to be a very promising result and plan for future work to assess the quantitative accuracy of CDFT-CI excited-state energetics against reference wave function-based calculations. In light of the accuracy of CDFT-CI ground-state energies and barrier heights,[9,10] we think that the method is very promising for excited states as well. Future work should be performed to test the robustness of the CDFT-CI method to the size of the AO basis set used and the exchange-correlation functional used for the underlying CDFT calculations. Deeper questions that remain include the sensitivity of the method to the mechanism for enforcing the constraints that define the diabatic states: does the promolecule prescription for modifying the density constraints produce universally better results than the constraints given from naïve chemical intuition? The CDFT-CI method also

makes an additional use of the weight (charge) prescription that is not present in ordinary CDFT, since it computes off-diagonal matrix elements of the constraining potential. The sensitivity of the couplings to the weight prescription should be further explored. Finally, if the predicted excited-state surfaces computed by CDFT-CI prove to be accurate and robust, it will be useful to implement analytic gradients for the CDFT-CI states, which will facilitate excited-state dynamics and the location of minimal-energy conical intersections.

[1] E. Runge and E. K. U. Gross, Phys. Rev. Lett. **52**, 997 (1984).

[2] M. E. Casida, C. Jamorski, K. C. Casida, and D. R. Salahub, J. Chem. Phys. **108**, 4439 (1998).

[3] C.-P. Hsu, S. Hirata, and M. Head-Gordon, J. Phys. Chem. A **105**, 451 (2001).

[4] P. Elliott, F. Furche, and K. Burke, Rev. Comput. Chem. **26**, 91 (2009).

[5] D. R. Yarkony, Rev. Mod. Phys. **68**, 985 (1996).

[6] B. G. Levine, C. Ko, J. Quenneville, and T. J. Martinez, Mol. Phys. **104**, 1039 (2006).

[7] C. W. Bauschlicher and S. R. Langhoff, J. Chem. Phys. **89**, 4246 (1988).

[8] Q. Wu and T. V. Voorhis, J. Chem. Theory Comput. **2**, 765 (2006).

[9] Q. Wu, C.-L. Cheng, and T. V. Voorhis, J. Chem. Phys. **127**, 164119 (2007).

[10] Q. Wu, B. Kaduk, and T. V. Voorhis, J. Chem. Phys. **130**, 034109 (2009).

[11] A. Dreuw and M. Head-Gordon, J. Am. Chem. Soc. **126**, 4007 (2004).

[12] N. T. Maitra, F. Zhang, R. J. Cave, and K. Burke, J. Chem. Phys. **120**, 5932 (2004).

[13] R. J. Cave, F. Zhang, N. T. Maitra, and K. Burke, Chem. Phys. Lett. **389**, 39 (2004).

[14] K. Giesbertz and E. Baerends, Chem. Phys. Lett. **461**, 338 (2008).

[15] S. Grimme and M. Waletzke, J. Chem. Phys. **111**, 5645 (1999).

[16] Q. Wu and T. Van Voorhis, Phys. Rev. A **72**, 024502 (2005).

[17] P. Bultinck, C. V. Alsenoy, P. W. Ayers, and R. Carbó-Dorca, J. Chem. Phys. **126**, 144111 (2007).

[18] A. Zangwill and P. Soven, Phys. Rev. A **21**, 1561 (1980).

[19] E. K. U. Gross and W. Kohn, Phys. Rev. Lett. **55**, 2850 (1985).

[20] Y. Shao, L. F. Molnar, Y. Jung, J. Kussmann, C. Ochsenfeld, S. T. Brown, A. T. Gilbert, L. V. Slipchenko, S. V. Levchenko, D. P. O'Neill, R. A. DiStasio, Jr., R. C. Lochan, T. Wang, G. J. Beran, N. A. Besley, J. M. Herbert, C. Y. Lin, T. V. Voorhis, S. H. Chien, A. Sodt, R. P. Steele, V. A. Rassolov, P. E. Maslen, P. P. Korambath, R. D. Adamson, B. Austin, J. Baker, E. F. C. Byrd, H. Dachsel, R. J. Doerksen, A. Dreuw, B. D. Dunietz, A. D. Dutoi, T. R. Furlani, S. R. Gwaltney, A. Heyden, S. Hirata, C.-P. Hsu, G. Kedziora, R. Z. Khalliulin, P. Klunzinger, A. M. Lee, M. S. Lee, W. Liang, I. Lotan, N. Nair, B. Peters, E. I. Proynov, P. A. Pieniazek, Y. M. Rhee, J. Ritchie, E. Rosta, C. D. Sherrill, A. C. Simonett, J. E. Subotnik, H. L. Woodcock III, W. Zhang, A. T. Bell, and A. K. Chakraborty, Phys. Chem. Chem. Phys. **8**, 3172 (2006).

[21] M. J. Frisch, G. W. Trucks, H. B. Schlegel *et al.*, GAUSSIAN 03, Gaussian, Inc., Wallingford, CT, 2004.

[22] A. D. Becke, J. Chem. Phys. **88**, 2547 (1988).

[23] A. J. C. Varandas, J. Chem. Phys. **107**, 867 (1997).