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Citation	Kaduk, Benjamin, and Troy Van Voorhis. "Communication: Conical Intersections Using Constrained Density Functional Theory–configuration Interaction." <i>The Journal of Chemical Physics</i> 133.6 (2010): 061102. Web.
As Published	http://dx.doi.org/10.1063/1.3470106
Publisher	American Institute of Physics
Version	Author's final manuscript
Citable link	http://hdl.handle.net/1721.1/70902
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Conical Intersections using Constrained DFT-Configuration Interaction

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May 6, 2010

1 Introduction

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 compute vertical excitation energies[1, 2, 3, 4]. The manifold of 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 the intersection provides an easy pathway for nonradiative decay, and the intersections 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 $\frac{dE}{dx}$ in the vicinity of the intersection[6]. In order to get a qualitatively correct treatment of CIs, multi-reference methods such as Complete Active Space (CAS), MRCI, and CASPT2 must be used[6]. Unfortunately, existing multi-reference treatments are almost universally wavefunction-based, and the computationally reasonable methods (such as CAS) have been shown to give only qualitatively-correct descriptions of multi-state energy-surface manifolds[7]; more accurate methods such as MRCI are frequently too expensive for use on real systems. We have developed a multi-reference DFT method, Constrained Den-

sity 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.

2 Methods

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 present)[11, 12, 13, 14]. As a Configuration-Interaction method, CDFT-CI introduces an active space of states, constructs a CI matrix of their energies and couplings, and diagonalizes that matrix, obtaining energies and coefficient vectors for the adiabatic states. This explicitly includes static correlation due to the multi-reference nature of the eigenstates, and the 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 that state’s Hamiltonian, enforcing a charge or spin constraint on some subset of the system of interest[15].

The CDFT equations rely on a partitioning of the system into multiple fragments, and a means for assigning (spin-) density to individual atoms [15, 16]. Thus, we write

$$W[\rho, \{V_k\}] = E[\rho] + \sum_k V_k \cdot \left(\sum_\sigma \int w_k^\sigma(\vec{r}) \rho_\sigma(\vec{r}) d\vec{r} - N_k \right) \quad (1)$$

where the V_k are lagrange multipliers that determine the actual constraint potentials $V_k w_k^\sigma$, and N_k is the target number of electrons (or spins) on the fragment defined by w_k . (For charge constraints, w_k^α and w_k^β will have the same sign; for spin constraints, they have opposite signs.) $E[\rho]$ is just the standard Kohn-Sham energy functional:

$$E[\rho] = \sum_\sigma \sum_i^{N_\sigma} \left\langle \phi_{i\sigma} \left| -\frac{1}{2} \nabla^2 \right| \phi_{i\sigma} \right\rangle + \int d\vec{r} v_n(\vec{r}) \rho(\vec{r}) + J[\rho] + E_{xc}[\rho^\alpha, \rho^\beta] \quad (2)$$

The CDFT states arise as the stationary functions of $W[\rho, \{V_k\}]$, satisfying $(F + \sum_k V_k w_k^\sigma(\vec{r})) \phi_{i\sigma} = \epsilon_{i\sigma} \phi_{i\sigma}$.

We take the time to note that the integer constraints that we might naïvely apply from our chemical intuition (e.g. $N = \pm 1$, $S = \frac{1}{2}$) 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 overlap of w_k for one fragment with the density tail from 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 w_k^g to determine the value of N_k that is 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 reference [9].

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

$$\begin{pmatrix} H_{11} & H_{12} & \cdots & H_{1N} \\ H_{21} & H_{22} & & H_{2N} \\ \vdots & & \ddots & \vdots \\ H_{N1} & H_{N2} & \cdots & H_{NN} \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_N \end{pmatrix} = E \begin{pmatrix} 1 & S_{12} & \cdots & S_{1N} \\ S_{21} & 1 & & S_{2N} \\ \vdots & & \ddots & \vdots \\ S_{N1} & S_{N2} & \cdots & 1 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ \vdots \\ c_N \end{pmatrix} \quad (3)$$

The diagonal elements of \mathbf{H} are just the energies of the constrained states that form the basis for the active space; the off-diagonal elements are constructed as

$$H_{12} = H_{21} = \frac{1}{2} \left[\left(E_1 + \sum_k V_{1,k} N_{1,k} + E_2 + \sum_k V_{2,k} N_{2,k} \right) \langle \Phi_1 | \Phi_2 \rangle - \sum_k V_{1,k} \langle \Phi_1 | w_{1,k} | \Phi_2 \rangle - \sum_k V_{2,k} \langle \Phi_1 | w_{2,k} | \Phi_2 \rangle \right] \quad (4)$$

where we add an extra index to the w , N , and V to account for the multiple states in the CI matrix. See reference [9] for the details of the derivation. 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 nonadiabatic couplings between them. (Note that these couplings as written are computed in a non-orthogonal basis, and are only useful in their own right after transformation to an orthogonalized basis.) 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 nuclear position.

Accordingly, we expect that the adiabatic states produced by diagonalization of the CDFT-CI matrix will accurately represent the true character of the ground *and excited* states of the system. 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 like 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]. This is particularly prone to failure in the vicinity of conical intersections, where the nature of the exact ground state rapidly changes 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.

3 Results

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 CASSCF calculations were performed using Gaussian 03[21]. For the CDFT calculations underlying the CDFT-CI framework, Becke populations[16] were used to determine the constraint values and potentials.

3.1 H₃

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 $R = 1.104 \text{ \AA}$ for B3LYP, $R = 1.198 \text{ \AA}$ for Full CI, and $R = 1.336 \text{ \AA}$ for CDFT-CI. We then held fixed two hydrogens on the y-axis and scanned over the x- and y-coordinates of the third hydrogen. 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 cone-like, 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 TD-DFT’s failures near the intersection, and how the CDFT-CI surfaces meet in a well-formed dual-lobed cone that reproduces the full CI result.

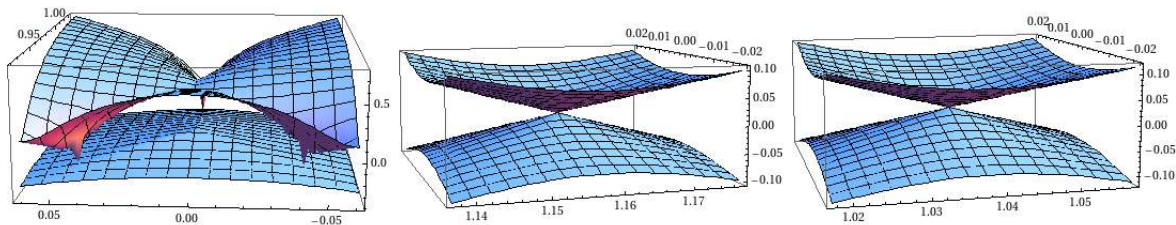


Figure 1: Triangular trihydrogen energy manifolds, as computed by TD-DFT (left), CDFT-CI (center), and full CI (right). Note the different energy scale for TD-DFT.

3.2 H₂O

Like H₃, 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 [22], we can accurately locate an intersection by scanning over symmetric linear geometries; in this case, we find an intersection at $R_{\text{O-H}} = 1.355465 \text{ \AA}$. Using this point as the center for our scan over the internal coordinates for the symmetric stretch and bend, we produce the plot on the left side of figure 2. Figure 2 shows very concretely the failure of TD-DFT to describe conical intersections, 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 . 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 diabatic constrained states for our basis, we must consider a different set of active states than for H₃ — the atoms in the system are no longer identical. In particular, we can make a covalent state with the oxygen atom a triplet ($S = \pm 1$) which is paired with a triplet “H₂” ($s = \mp 1$). We also include the two ionic states OH⁻/H⁺ and H⁺/OH⁻, for a total of four states in the active space. 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 near the intersection.

4 Discussion

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 “H₂”

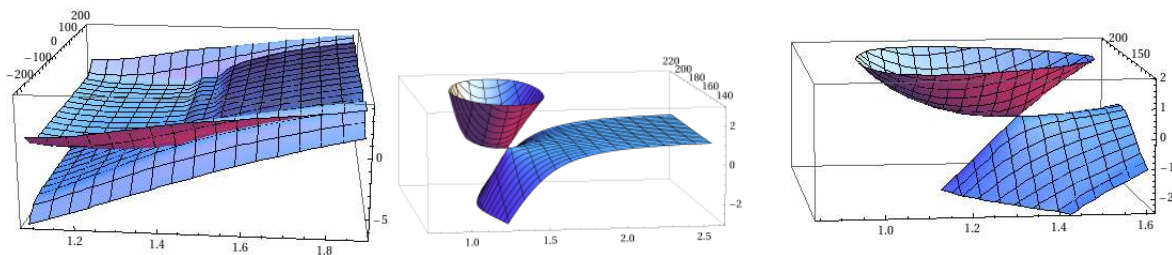


Figure 2: Symmetric water energy manifolds, as computed by TD-DFT (left), CDFT-CI (center), and CAS(6,6) (right)

produced a conical intersection at the unphysical $R_{\text{O-H}}$ of 0.94 Å! This active-space dependence is similar to the behavior of Complete Active Space wavefunction 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 failed to yield an intersection at all. Experimentation and/or prior knowledge of the nature of the states of interest will be needed in order to perform reliable CDFT-CI calculations. We expect that to some extent this can be avoided by using a larger active space as can be done with MCSCF; it has not been necessary for the small systems considered in this work. However, the need for such a “brute force” approach of using more states in the active space should be tempered in CDFT-CI, since the nature of the states used is not forced by the nature of the SCF, and can instead be selectively chosen by the constraint potential.

5 Conclusions

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 wavefunction-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, in computing the coupling elements between states. The sensitivity of the couplings to the weight prescription should also be further explored. 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.

6 Acknowledgements

This work was supported by an NSF-CAREER Award (CHE-0547877). T.V. gratefully acknowledges a Packard Fellowship.

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